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# CATALYSIS

Inorganic and Organic

BY  
*et*  
SOPHIA BERKMAN, JACQUE C. MORRELL  
and GUSTAV EGLOFF

UNIVERSAL OIL PRODUCTS COMPANY  
RESEARCH LABORATORIES  
CHICAGO, ILLINOIS


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## Preface

Catalysis, including inorganic and organic reactions in both pure and applied science, has been studied intensively for more than a hundred years. The fact that many modern chemical processes and industries are based on the use of catalysts clearly emphasizes the importance of a thorough knowledge of the subject of catalytic chemistry.

Attempts have been made to interpret experimental results, and there are many different viewpoints on the mechanism of catalysis. Some of these have crystallized into hypotheses which, however, are justified in a few instances only; none of them has evolved into a general theory of catalysis. The complexity of the phenomenon of catalysis at the present time does not permit the application of a single theory unequivocally to various types of catalytic reactions. In order to arrive at an understanding of catalysis, it seemed logical in the present work to arrange the findings of the various workers in the field and their original interpretations into a systematic presentation of the subject with some consideration of its historical evolution. The book has been divided into chapters, each pertaining to a particular branch of the field significant in itself and at the same time related to the general subject of catalysis. This will permit the reader to acquire a knowledge of each specific branch of the subject and perhaps to visualize a logical thread running through the field of catalytic chemistry, thereby simplifying and facilitating a critical analysis of the available experimental facts.

It is the belief of the authors that future research in the field of catalysis may be logically derived from the systematically presented facts instead of from the empirical methods used at present. New experiments, taking into consideration the vast number of observations outlined in the present book, may lead the future investigator to justified generalizations in catalytic chemistry.

The authors wish to express their appreciation and thanks to Dr. H. H. Wenzke for helpful suggestions, and to Miss Eugenia Lieboner (M.Sc.) in the preparation of the typewritten manuscript and for proof-reading.

SOPHIA BERKMAN  
J. C. MORRELL  
GUSTAV EGLOFF

Chicago, Illinois  
Dec. 1, 1939

Dedicated to  
VLADIMIR N. IPATIEFF  
Pioneer in Catalytic Reactions

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**CHAPTER 11. CATALYSIS IN THE PETROLEUM INDUSTRY**

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# Chapter 1

## The Phenomenon of Catalysis

### Introduction

Although catalysis in both organic and inorganic reactions was recognized more than a hundred years ago, our knowledge of catalytic phenomena is today still largely uncoordinated. Early explanations attributed the remarkable changes in chemical activity effected by mere contact with certain substances to a force unique to those substances. This "catalytic" force<sup>13</sup> was believed to influence the polarity of atoms or to cause changes in the movement of molecules or the atoms composing them. Substances possessing this force were called catalysts. They were supposed to produce, through their presence only and not by "affinity," an arrangement in which greater electro-chemical neutralization was possible.<sup>58</sup> The modern interpretation of this concept<sup>57</sup> associates catalytic action with the formation of more stable compounds, limiting it to reactions thermodynamically possible.

Catalysts may be characterized best by defining their properties. They do not contribute energy to a reaction or change the equilibrium point of reversible reactions.<sup>58, 59</sup> They do not initiate reactions,<sup>59</sup> but have an accelerating effect<sup>13, 59</sup> which, when combined with selectivity, may result in the ability to direct reactions.<sup>13, 70</sup> In addition to these general properties, catalysts may also have the ability of entering into a reaction over and over again<sup>41</sup> by self-regeneration<sup>41, 59</sup> so that the catalyst is unchanged on completion of the reaction, small amounts of the catalyst thus being able to transform large quantities of the reacting substances.<sup>59</sup>

In the description of catalysis as a physico-chemical phenomenon, three factors should be considered: (a) the course of the catalytic reaction; (b) the mechanism by which this course is maintained; and (c) the specific properties of the catalyst which determine this mechanism.

The course of a reaction may be altered by the influence of the catalyst on the velocity, or rapidity in approaching the equilibrium state; on the chemical composition and yield of the final product, through selective catalysis where alternative reactions are possible; and on the physical conditions, such as temperature and pressure, under which the reaction takes place.

The mechanism by which a catalyst functions depends upon the type of reaction in which it takes part. The mode of action of the catalyst may be largely chemical, or the catalyst may have a purely physical effect; and in some cases both types of influence may be exerted. An attempt is made to correlate the actions and effects of catalysts with their specific properties.

### Intermediate Compound Formation

The acceleration of a chemical change by a catalyst through the alternate formation and decomposition of compounds between the catalyst and the reactants is one of the chemical views of the mechanism of catalysis. These intermediate compounds are sufficiently labile to decompose readily, yielding the reaction product and the regenerated catalyst.

The hypothesis of intermediate compound formation traces its origin as far back as 1808;<sup>28</sup> Clement and Désormes proposed this type of mechanism for the old method of sulfuric acid catalysis by means of nitric oxide. Dobereiner (1824) observed a similarity in the action of nitric oxide with that of platinum in the oxidation of alcohol to acetic acid. Hennell (1828) and Liebig (1834) proved that ethyl sulfuric acid was an intermediate compound in the formation of ethyl ether. It was assumed that the proposed intermediate compound hypotheses, in order to be reliable, must answer definite requirements: (1) the rate of formation and decomposition of the intermediate compounds must be greater than that of the uncatalyzed reaction; (2) the catalyst is not performing a purely physical function, and (3) the intermediate compound is sufficiently unstable to decompose under existing conditions with the formation of new products. The main objection against the intermediate compound hypothesis is that in many cases the intermediates if formed can not be isolated due to the high velocities with which chemical changes proceed in catalyzed systems, as well as to the difficulty of analysis of labile intermediate compounds. The fact that a compound can be isolated by altering the conditions under which a reaction proceeds can not be considered as conclusive proof that the compound so isolated is necessarily an intermediate in the catalytic reaction.

A catalyst has been supposed to act chemically also by splitting up a chemical reaction into several intermediate ones. Henri, De la Rive, Kuhlmann and Mercer assumed intermediate processes in the catalytic synthesis of hydrogen and oxygen, postulating alternate oxidation and reduction of the catalyst as the mechanism; but Berzelius doubted this explanation because of its lack of general applicability to all types of catalysis. Ostwald believed that catalysis might proceed through "intermediate reactions" but that actual proof was necessary in particular cases by the measurement of the velocities of the intermediate reactions, and the comparison of the resultant of these with the over-all reaction velocity. In the opinion of Schönbein, a catalyst may be instrumental in altering the nature of the sequence of "intermediate states" by which, according to Ostwald, every chemical reaction proceeds best.

The intermediate compounds, reactions and states which have been assumed for some reactions and actually found in others, are summarized in Tables 1 to 6 inclusive. These tables show examples of these factors in the behavior of catalysts for reactions of synthesis, decomposition, oxidation and hydrogenation.

It will be seen from the foregoing tables that many types of compounds have been postulated as the intermediates in various reactions. In oxidation processes, unstable oxides or peroxides are believed to be formed; in

(Text continued on page 16)

Table 1. Intermediate Compounds or Reactions in Catalytic Synthetic Reactions.

Reaction	Catalyst	Intermediate Reactions	Intermediate Compound	Observer
Synthesis of $\text{H}_2\text{O}$ from $\text{O}_2$ and $\text{H}_2$ .	Pt sponge.		First an oxide of Pt formed which is reduced by $\text{H}_2$ , yielding $\text{H}_2\text{O}$ and the original metal.	Sabatier: <i>La Catalyse en Chimie Organique</i> , 60 (1920).
Synthesis of $\text{H}_2\text{O}$ from $\text{O}_2$ and $\text{H}_2$ .	Cu.	Alternate oxidation and reduction of the metal.		Pease and Taylor: <i>J. Am. Chem. Soc.</i> , <b>44</b> , 1637 (1922).
Synthesis of $\text{H}_2\text{O}$ from $\text{O}_2$ and $\text{H}_2$ .	Reduced Ni.			Benton and Emmett: <i>J. Am. Chem. Soc.</i> , <b>48</b> , 632 (1926).
Synthesis of $\text{NH}_3$ .	Iron synthetic ammonia catalysts ( $\text{Al}_2\text{O}_3$ and/or $\text{K}_2\text{O}$ used as promoters).	$2 \text{Fe} + 1/2 \text{N}_2 = \text{Fe}_3\text{N}$ $3/2 \text{H}_2 + 3\text{Fe}_3\text{N} = 2\text{Fe}_3\text{N} + \text{NH}_3$ $3/2 \text{H}_2 + \text{Fe}_3\text{N} = 3\text{Fe} + \text{NH}_3$	30–70% $\text{Fe}_3\text{N}$ and 70–100% $\text{Fe}_3\text{N}$ or $\text{Fe}_3\text{N}$ ; decomposition of $\text{Fe}_3\text{N}$ as compared with that of $\text{Fe}_2\text{N}$ and $\text{Fe}_3\text{N}$ is autocatalytic; $\text{Fe}_3\text{N}$ in an active catalyst decomposes faster than in one less active.	Emmett and Love: <i>J. Am. Chem. Soc.</i> , <b>55</b> , 4043–4050 (1933).
Synthesis of $\text{CH}_4$ from $\text{CO}$ and $\text{H}_2$ .	Ni.		$\text{Ni}_3\text{C}$ assumed to be the intermediate compound.	Bahr and Bahr: <i>Ber.</i> , <b>61B</b> , 2177, 2465 (1928).
Synthesis of aromatic hydrocarbon ketones and di- and triphenylmethane derivatives.	$\text{AlCl}_3$ .		Well-defined addition compounds formed not only with acyl chlorides but also with numerous other compounds.	Menschutkin: <i>J. Chem. Soc. (Abstracts)</i> 96, 897 (1909); 275, 532 (1911); 160 (1912). Perrin: <i>Ber.</i> , <b>33</b> , 815 (1900). Gustavson: <i>Comp. rend.</i> , <b>36</b> , 1065 (1903); <b>140</b> , 940 (1905).



Table 2. Intermediate Compounds or Reactions in Catalytic Decomposition Reactions.

Reaction	Catalyst Alkalies and alkaline earths.	Intermediate Reactions	Intermediate Compound formed.	Observer
Decomposition of $\text{H}_2\text{O}_2$ .				Schöne: <i>Ann.</i> , 192, 257 (1878); 193, 241 (1878). Berthelot: <i>Ann. chim. phys.</i> (5), 21, 153 (1880).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{Co}_2\text{O}_3$ , $\text{NiO}$ .	The catalyst reacts with $\text{H}_2\text{O}_2$ , $\text{O}_2$ being evolved from both; Co re- turns to a lower oxide which is then oxidized to cobalt peroxide; if nickel peroxide is prepared in- dependently (does not originate in the reaction) it reacts with $\text{H}_2\text{O}_2$ ; similar to the cobalt salt.	Cobalt oscillates in its changes between $\text{Co}_2\text{O}_3$ and $\text{CoO}$ .	Bayley: <i>Phil. Mag.</i> (5), 7, 126 (1879).
Decomposition of $\text{H}_2\text{O}_2$ .	Hg.		Intermittent formation of a film of mercuric peroxide.	Bredig and von Antropoff: <i>Z. Elektr.</i> , 12, 585 (1906). von Antropoff: <i>J. prakt.</i> <i>Chem.</i> (2), 77, 273 (1908).
Decomposition of $\text{H}_2\text{O}_2$ .	Iron salts.	$\text{H}_2\text{FeO}_4 + \text{H}_2\text{O}_2 = \text{H}_2\text{FeO}_3 +$ $\text{H}_2\text{FeO}_3 + \text{H}_2\text{O}_2 = \text{H}_2\text{FeO}_4 + \text{H}_2\text{O}$	$\text{H}_2\text{FeO}_4$ (deduced from meas- urements of adsorption spectra for $\text{H}_2\text{O}_2$ mixed with Fe salts).	Bohnson and Robertson: <i>J.</i> <i>Am. Chem. Soc.</i> , 45, 2439 (1923). Goard and Rideal: <i>Proc. Roy.</i> <i>Soc. (A)</i> , 105, 148 (1932).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{Na}_2\text{MoO}_4$ or $\text{Na}_2\text{MoO}_4$ $\text{WO}_4^{2-}$ , $\text{Cr}_2\text{O}_7^{2-}$ , $\text{Cu}(\text{OH})_2$ , $\text{Fe}^{2+}$ are supposed to act according to the same mechanism.	Two phases in the reaction: (1) tran- sition of O atoms from $\text{H}_2\text{O}_2$ mole- cules to the catalyst molecule with formation of the intermediate com- plex ( $\text{FeO}_3$ ); (2) intermolecular recombination of active O atoms in $\text{FeO}_3$ molecules with regenera- tion of the catalyst molecules.	$\text{Na}_2\text{MoO}_3 \cdot \text{H}_2\text{O}$ : complex dis- sociates into $\text{MoO}_4^{2-}$ and $\text{H}_2\text{O}$ ; $\text{Na}_2\text{MoO}_3 \cdot \text{H}_2\text{O}$ dis- sociates into $\text{MoO}_4^{2-}$ , $\text{MoO}_3$ , and $\text{MoO}_4^{2-}$ .	Kobosew and Ssokolow: <i>Chim. Sh. fizich Khimii</i> , 4, 275-294 (1933).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{Na}_2\text{WO}_4 + \text{FeSO}_4$ .		$\text{Na}_2\text{WO}_4$ isolated is quite stable in an acid solution but decomposes on adding $\text{FeSO}_4$ .	Konowalowa: <i>Z. anorg. allg.</i> <i>Chemie</i> , 222, 81-91 (1935).
Decomposition of $\text{H}_2\text{O}_2$ .	Ferrous and ferric salts.	$\text{Fe}^{2+} + \text{H}_2\text{O}_2 = \text{Fe}^{3+} + \text{OH}^- + \text{OH}$ $\text{OH} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{HO}_2$ $\text{HO}_2 + \text{H}_2\text{O}_2 = \text{O}_2 + \text{H}_2\text{O} + \text{OH}$ $\text{OH} + \text{Fe}^{3+} = \text{Fe}^{2+} + \text{OH}$	$\text{HO}_2$ .	Haber and Weiss: <i>Proc. Roy.</i> <i>Soc. London (A)</i> , 147, 332- 351 (1934).
Decomposition of $\text{H}_2\text{O}_2$ .	Hydrochloric acid-chlo- ride solution; $\text{HCl}$ (2.84 to 5.86 n).	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{Cl}^- = \text{Cl}_2 + 2\text{H}_2\text{O}$ $\text{H}_2\text{O}_2 + \text{Cl}_2 = \text{O}_2 + 2\text{H}^+ + 2\text{Cl}^-$	$\text{Cl}_2$ .	Makower: <i>J. Am. Chem. Soc.</i> , 56, 1315-1319 (1934).

Decomposition of $\text{NH}_3$ .	Tungsten surface.		Tungsten adsorbs $\text{H}_2$ and $\text{NH}_3$ in a normal manner, but $\text{N}_2$ forms a surface compound.	Bodenstein: <i>Z. Phys. Chem.</i> (Bodenstein Fed. Bond), 593-607 (1931).
Decomposition of $\text{NH}_3$ .			In the first stage of the catalytic decomposition tungsten nitride or tungsten imide is formed as a surface product.	Frankenburger and Hodler: <i>Trans. Far. Soc.</i> , 28, 229 (1932).
Decomposition of hypochlorites.	Cobalt oxide.		Cobalt passes through intermediate compounds from $\text{Co}_2\text{O}_3$ to $\text{CoO}$ .	Bayley: <i>Phil. Mag.</i> (5), 7, 126 (1879).
Dry decomposition of $\text{KClO}_3$ .	$\text{MnO}_2$ .	$9\text{MnO}_2 + 2\text{KClO}_3 \xrightarrow{\text{Mn}} 3[(\text{MnO}_4)_2\text{Mn}] \rightarrow 9\text{MnO}_3 + 3\text{O}_2$		Denis: <i>Bull. Trav. Soc. Pharm. Bordeaux</i> , 74, 93-112 (1936).
Decomposition of $\text{N}_2\text{O}_5$ .	$\text{O}_2$ .	$\begin{aligned}\text{N}_2\text{O}_5 &= 2\text{NO}_2 + \frac{1}{2}\text{O}_2 \\ \text{NO}_2 + \text{O}_3 &= \text{NO}_3 + \text{O}_2 \\ 2\text{NO}_2 &= 2\text{NO} + \text{O}_2 \\ \text{NO}_2 + \text{NO}_2 &= \text{N}_2\text{O}_4\end{aligned}$	$\text{NO}_2$ .	White and Tolman: <i>J. Am. Chem. Soc.</i> , 47, 1240 (1925). Schumacher and Spinger: <i>Z. Phys. Chem.</i> , 136 A, 77 (1928). Nordberg: <i>Science</i> , 70, 580 (1929).
Decomposition of $\text{N}_2\text{O}_4$ .	$\text{Cl}_2$ .	$\begin{aligned}\text{Cl}_2 + \text{O}_2 &= \text{ClO} + \text{ClO}_2 \\ \text{ClO}_2 + \text{O}_2 &= \text{ClO}_3 + \text{O}_2 \\ \text{ClO}_3 + \text{O}_2 &= \text{ClO}_4 + 2\text{O}_2 \\ 2\text{ClO}_2 &= \text{Cl}_2 + 3\text{O}_2 \\ 2\text{ClO} &= \text{Cl}_2 + \text{O}_2\end{aligned}$	$\text{ClO}_2$ $\text{ClO}_3$ $\text{ClO}$	Bodenstein, Padelt and Schumacher: <i>Z. Phys. Chem. B</i> , 5, 209 (1929).
Decomposition of ozone.	$\text{Br}_2$ .			Schumacher: <i>Trans. Electrochem. Soc.</i> , 71, Preprint 26, 16 pp. (1937).
Decomposition of $\text{H}\cdot\text{CHO}$ .	Metals of the Pd group.		A series of intermediate compounds.	Müller and Müller: <i>Z. Elektrochem.</i> , 31, 41 (1925).
Decomposition of alcohol.	$\text{PtO}_2$ .		A series of normal and acid phosphates; acid phosphates formed, decompose; definite chemical compounds formed as intermediate products which partially dissociate with increase in temperature.	Balarew: <i>J. prakt. Chem.</i> , 104, 368 (1922); <i>To the Knowledge of Catalysis</i> , 158, 105 (1926).
Decomposition of aldehydes.	I $_2$ .	$\begin{aligned}\text{RCHO} + \text{I}_2 &= \text{RI} + \text{HI} + \text{CO} \\ \text{RI} + \text{HI} &= \text{I}_2 + \text{RH} \\ \text{R} &= \text{CH}_3, \text{C}_6\text{H}_5\end{aligned}$	RI, HI.	Rollefson and Pauli: <i>J. Am. Chem. Soc.</i> , 59, 625 (1937).

Table 2 (Continued).

Reaction	Catalyst	Intermediate Reactions	Intermediate Compound	Observer
Decomposition of acetaldehyde and ethylene oxide; T. 300° and 500°.	Material of which the container is made.	1. $C_2H_4O = CH_2 + CO$ 2. $2C_2H_4O = CH_3 - CH = CH - CHO + H_2O$ $CH_3 - CH = CH - CHO \rightarrow CH_3 - CH = CH_2 + CO$ Process 1. dominates in container without the catalyst; Process 2. dominates in container filled with the material of the container.	The primary product converts irreversibly into an unstable intermediate product which splits within the time $\Delta t$ in the gas phase according to reaction 1. or 2.	Travers and Seddon: <i>Nature</i> , 137, 906-907 (1936).
Decomposition of diethyl ether; reaction interpreted by 3. processes occurring side by side: (1) molecular rearrangement; (2) formation of free radicals from diethyl ether, and (3) introduction of a chain reaction leading to decomposition of aldehyde.	Small amounts of ether accelerate decomposition of acetaldehyde.		Acetaldehyde.	Fletcher and Rollefson: <i>J. Am. Chem. Soc.</i> , 58, 2129-2135 (1936).
Decomposition of dimethyl ether.		$C_2H_5 + NO \rightarrow (X)$ $\rightarrow CH_3NH_2 + CO$	Formaldoxime.	Thompson and Meissner: <i>Nature</i> , 139, 1018-1019 (1937).

Table 3. Intermediate Compounds or Reactions in Catalytic Oxidation Reactions.

Reaction	Catalyst	Intermediate Reaction	Intermediate Compound	Observer
Manufacture of $\text{H}_2\text{SO}_4$ .	NO.	$2\text{NO} + \text{O}_2 = 2\text{NO}_2$ $\text{NO}_2 + \text{SO}_2 + \text{H}_2\text{O} = \text{NO} + \text{H}_2\text{SO}_4$ $2\text{HNO}_2 + \text{SO}_2 = \text{H}_2\text{N}_2\text{SO}_4$ $\text{H}_2\text{N}_2\text{SO}_4 = 2\text{NO} + \text{H}_2\text{SO}_4$ $2\text{NO} + \text{O}_2 = \text{N}_2\text{O}_4$ $2\text{N}_2\text{O}_4 + 2\text{H}_2\text{SO}_4 = 2\text{H}_2\text{N}_2\text{SO}_4 + \text{O}_2$	$\text{NO}_2$ $\text{N}_2\text{O}_4$ $\text{H}_2\text{N}_2\text{SO}_4$ , $\text{H}_2\text{N}_2\text{SO}_3$ $\text{H}_2\text{N}_2\text{SO}_4$	Peligot: (1844). Berzelius: (1845). Dumas: (1847). Davy: (1812). Raschig: (1811).
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ .	$\text{V}_2\text{O}_5$ .	Conversion of $\text{V}_2\text{O}_5$ to $\text{VOSO}_4$ by passing $\text{SO}_2$ and air over pure $\text{V}_2\text{O}_5$ at $450^\circ$ ; formation of $\text{VOSO}_4$ could not be ascertained.		Neumann: (Refer to C. 1934 I 5). Siegert: <i>Angew. Chem.</i> , 50, 319-320 (1937). Siegert: <i>Chem. Fabrik</i> , 26, 1-11 (1937).
Oxidation of $\text{SO}_2$ .		$12\text{Fe}_2\text{O}_3 + 4\text{SO}_2 = 8\text{Fe}_2\text{O}_4 \cdot 4\text{SO}_4$ $8\text{Fe}_2\text{O}_4 \cdot 4\text{SO}_2 = 7\text{Fe}_2\text{O}_4 + \text{Fe}_2(\text{SO}_4)_4$ $\text{Fe}_2(\text{SO}_4)_4 = \text{Fe}_2\text{O}_4 + 4\text{SO}_2$ $8\text{Fe}_2\text{O}_4 + 2\text{O}_2 = 12\text{Fe}_2\text{O}_3$ $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 + 2\text{O}_2 = 4\text{SO}_2$	Ferro-ferric sulfate.	Neumann, B. and Heintke: <i>Z. Elektrochem.</i> , 43, 246 (1937).
Oxidation of $\text{NH}_3$ by persulfate.	Ag.		Trivalent Ag ion active in oxidation.	Jost: <i>J. Am. Chem. Soc.</i> , 48, 374 (1926).
Oxidation of $\text{NH}_3$ to nitric oxide and free $\text{N}_2$ in proportions varying with experimental conditions.	Hot Pt gauze.	$\text{HNO}$ and undecomposed $\text{NH}_3$ react.	Distinct change in appearance of Pt from bright to a dull; formation of intermediate labile compounds.	Andrussow: <i>Z. ang. Chem.</i> , 39, 321 (1926); 40, 166 (1927); 41, 205 (1928); <i>Ber.</i> , 59, 458 (1926); 60, 536, 2005 (1927); Bodenstein: <i>Z. ang. Chem.</i> , 40, 174 (1927).
Oxidation of $\text{NH}_3$ .		Formation of $\text{NH}_4$ .		Raschig: <i>Z. ang. Chem.</i> , 40, 1183 (1927); 41, 207 (1928); Hofmann: <i>Ber.</i> , 50, 204 (1926); 60, 1190 (1927); 62, 2509, 3000 (1929); Neumann and Manke: <i>Z. Elektrochem.</i> , 35, 751 (1929).
Oxidation of $\text{NH}_3$ to 90% $\text{N}_2\text{O}$ .	$\text{MnO}_2 + \text{Bi}_2\text{O}_3$ .	At low temperature. $2\text{HNO} = \text{N}_2\text{O} + \text{H}_2\text{O}$ . At high temperature, $\text{HNO}$ is oxidized to $\text{HNO}_2$ and $\text{NO}$ .		Nagel: <i>Z. Elektrochem.</i> , 36, 754 (1930).

Table 3 (Continued).

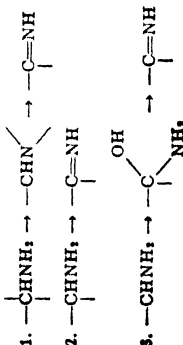
Reaction	Catalyst	Intermediate Reaction	Intermediate Compound	Observer
Oxidation of $\text{NH}_3$ - $\text{CH}_3$ mixture to $\text{HCN}$ ; $\text{NH}_3 + 3\text{O}_2 + 2\text{CH}_4 = 2\text{HCN} + 6\text{H}_2\text{O}$ .	Pt.	The intermediate step is the formation of $\text{HNO}$ and/or $\text{NH}_2\text{O}$ ; complex which acts on the catalyst, oxidizing the $\text{NH}_3$ with the formation of a di-imide ( $\text{N}_2\text{H}_2$ ) or, on further oxidation, to $\text{N}_2$ .	Intermediate compounds, methylenimine( $\text{CH}_2$ ), $\text{NH}_2$ , and methylenamine ( $\text{CH}_2$ ). $\text{NH}_3$ could be isolated up to 80-90% using an inert catalyst Cu at 300°.	Andrussow: <i>Ang. Chem.</i> , <b>48</b> , 593-595 (1935).
Oxidation of $\text{NH}_3$ by $\text{O}_2$ at low pressures, 0.02 mm. Hg; streaming velocity 2-2.6 $\times 10^{-4}$ mol/hr.; $\text{NH}_3$ ; $\text{O}_2=1:2.2$ or 2:1; $\text{N}_2$ is the only gaseous reaction product.	Pt wire (electrically heated).		$\text{NH}_4\text{O}$ (it is stated that N and $\text{N}_2\text{H}_4$ cannot occur for thermodynamic reasons); previously assumed $\text{NH}$ as intermediate product is less probable than $\text{NH}_2\text{O}$ .	Bodenstein: <i>Trans. Electrochem. Soc.</i> , <b>71</b> , Preprint 25, 20 pp. (1937); (Refer to C. 1935 II 2624). Bodenstein and Battner: <i>Congr. intern. quim. pura aplicada</i> (9th Congt. Madrid), <b>3</b> , 475-494 (1934).
Oxidation of Co by $\text{H}_2\text{O}$ .	Ferroso-ferric oxide ( $\text{Fe}_2\text{O}_3$ ), Co, Mn and Ag oxides.	Alternate or simultaneous reduction and oxidation of ferroso-ferric oxide to ferrous oxide or Fe by CO.		Armstrong and Hilditch: <i>Proc. Roy. Soc.</i> , <b>97A</b> , 266 (1920).
Oxidation of $\text{C}_2\text{H}_5\text{OH}$ to $\text{CH}_3\text{COOH}$ and $\text{C}_2\text{H}_4$ to $\text{CO}_2$ and $\text{H}_2\text{O}$ ; oxidation of $\text{CH}_3\text{OH}$ .	Charcoal on which oxygen is adsorbed; C catalyst acts as a carrier of $\text{O}_2$ .	Calvert points out that these reactions are not due to any known oxide of carbon formed in the intermediate stage.	Characteristic cyclic variations in color of copper surface indicating a continuous change in the state of oxidation of copper.	Calvert: <i>J. Chem. Soc.</i> , <b>20</b> , 293 (1867).
Oxidation of alcohol by air.	$\text{OsO}_4$ .	Air oxidizes osmium dioxide to osmium tetroxide, the latter oxidizing alcohol; two stages of the reaction assumed, indicating the formation of intermediate compounds.		Hofmann: <i>Ber.</i> , <b>45</b> , 3329 (1912); <b>46</b> , 1659, 2834 (1913).
Oxidation of alcohol.	Fe.		Formation of ferric acid assumed as an intermediate product.	Walter and Christensen: <i>J. Am. Chem. Soc.</i> , <b>48</b> , 11, 2083 (1926).
Oxidation processes.	Pt.	$\text{Pt} + \text{O}_2 = \text{PtO}_2 + 2(\text{A}) = 2(\text{A})\text{O} + \text{Pt}$ (A, substance oxidized).	Unstable peroxides; the peroxide of Pt was not isolated as an intermediate compound, but the oxides of platinum, $\text{PtO}_2$ and $\text{PtO}$ were found to dissociate with a rise in temperature at 800°.	Dupré, Wenger and Ufer: <i>Helv. Chim. Acta</i> , <b>8</b> , 669 (1925).

Oxidation of tartaric or formic acid by  $\text{H}_2\text{O}_2$ .  $\text{Fe}^{++}$ .

Oxidation reactions.

Oxidation of naphthalene to phthalic acid by air or oxygen.  $\text{MnO}_2$ ,  $\text{V}_2\text{O}_5$ .

Oxidation of bornyl amine with  $\text{O}_2$  in isopropyl alcohol as solvent to form camphor and a small amount of bornylene; 1, 30-55°; the conversion of bornyl amine to camphor amine may proceed through different reactions, the third direction being assumed most plausible:



In reaction between  $\text{Fe}^{++}$  and  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{+++}$  is formed; a complex is formed between the oxygen donor and the oxidizable substance.

A derivative of  $\text{Fe}^{+++}$  acts as an oxygen donor (during the reaction between  $\text{Fe}^{+++}$  and the oxidizable substance no reduction to  $\text{Fe}^{++}$  takes place).

Peroxides formed immediately catalyzed the oxidation reactions.

Alternate reduction and oxidation of the catalyst which oxidizes naphthalene and is itself reoxidized by air.

Camphor oxime and camphor imine (the latter oxidizes to camphor azine:  $2\text{C}_{10}\text{H}_{15}\text{NH} + \text{O} = \text{C}_{10}\text{H}_{15}\text{N} - \text{NC}_{10}\text{H}_{15} + \text{H}_2\text{O}$ ) (the possibility of camphor oxime being the intermediate product is excluded).

Dempster and Stirling: *Bioch. J.*, 28, 1048-1062 (1934).

Pretrre: *Ann. combustibles liquides*, 7, 699 (1932).  
Dumanois: *Compt. rend.*, 197, 393 (1933).

Marek and Hahn, "Catalytic Oxidation of Organic Compounds in Vapor Phase," Chemical Catalog Co., New York, 1932.

E. I. DuPont de Nemours & Co.: U.S.P. 1,515,299, and U.S.P. 1,599,228.

Demjanow and Lenarski: *Izv. Akad. Nauk U.S.S.R.*, 1001-1013 (1937).

Table 4. Intermediate Compounds or Reactions in Catalytic Hydrogenation Reactions.

Reaction	Catalyst	Intermediate Reactions	Intermediate Compound	Observer
Reduction of nitrates to nitrites; chlorates to chlorides; ferric salts to ferrous salts; mercuric to mercurous; indigo blue to indigo white; sulfur dioxide to hydrogen sulfide; arsenic trioxide to arsenic; benzoyl chloride to benzaldehyde; nitrobenzene to aniline.	Pd; in general, Pd is not so good a catalyst for hydrogenation as Pt because it does not give off its hydrogen as rapidly as Pt.		A definite complex between Pd and H <sub>2</sub> is formed in the cold. PdH <sub>2</sub> hydrogen adsorbed on Pd does reduce and forms H <sub>2</sub> O when placed in contact with atmospheric oxygen.	Sabatier: <i>La Catalyse</i> #8 <i>Chimie Organique</i> , 60, 49-66 (1920); "Catalysis in Organic Chemistry," p. 165 (New York), D. van Nostrand Co., 1923. Dewar: <i>Chem. News</i> , 76, 274 (1897). Gladstone and Tribe: <i>Chem. News</i> , 37, 68 (1898). Kolbe and Zastoff: <i>J. prakt. Chem.</i> (2), 4, 418 (1871).
Hydrogenation processes.	Finely dispersed Pt, Ni, Cu	$\text{Pt} + \text{O}_2 = \text{Pt} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array}$ $\text{Pt} + \text{H}_2 = \text{Pt} \begin{array}{c} \diagup \text{H} \diagdown \\ \diagdown \text{H} \diagup \end{array}$	Oxygen must be present for hydrogenation to take place; unstable hydrides are formed on the surface of these metals; Pt combines with oxygen first to form a sort of peroxide which then unites with the hydrogen; this peroxide is the active intermediate compound passing its hydrogen on to the substance to be hydrogenated.	Willstätter and Waldschmidt-Leitz: <i>Ber.</i> , 54, 120 (1921).
Hydrogenation of acetylene derivatives (glycols, alcohols, etc.).				Salkind: <i>Z. phys. Chem.</i> , 104, 177 (1923).
Hydrogenation of aliphatic ethylene compounds.	Pt black.		The unstable intermediate product is an adsorption compound between the catalyst and the unsaturated molecule.	Lebedev, Koblinsky and Jakubchik: <i>J. Chem. Soc.</i> , 127, 417 (1925).
Hydrogenation of organic compounds, e.g., ethylene.	Finely dispersed Ni.	$\text{H}_2 + \text{Ni}_2 = \text{Ni}_2\text{H}_2$ $\text{Ni}_2\text{H}_2 + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_6 + \text{Ni}_2$ $\text{Ni}_2\text{H}_2 \text{ or } \text{Ni}_2\text{H}_4; \text{ if the hydride theory is true, then such catalysts give off "atomic" hydrogen which is more active than the molecular variety.}$	Temporary hydrides, NiH <sub>2</sub> and NiH <sub>4</sub> from which H <sub>2</sub> is given off to the organic compound.	Sabatier: <i>Ind. Eng. Chem.</i> , 18, 1005 (1926).

Hydrogenation of unsaturated compounds.	Ni.	It is assumed that in the mechanism of the reaction Ni attaches itself in some way to the unsaturated carbons $-\text{HC}=\text{CH}-$ while the $\text{H}_2$ and the fatty oil are both coupled with the Ni; interaction brought about by the presence of electrolytes in the system.	Both the unsaturated compound and the $\text{H}_2$ form labile compounds with Ni; formation of the ternary, unspecified, unstable complex of Ni with the unsaturated fat and $\text{H}_2$ breaks down into a saturated or more saturated fat and Ni.	Armstrong and Hilditch: <i>Proc. Roy. Soc.</i> , <b>98A</b> , 37 (1920).
Hydrogenation of organic compounds.	Ni, Fe.	Bredig showed that $\text{NiH}_2$ does not hydrogenate the double bonds or the benzene ring; he found also that Pt, Pd, Ni catalysts prepared with glow discharge were inactive for the hydrogenation of ethylene; but when oxygen is substituted for hydrogen, very active surfaces are obtained.	Evidence obtained in support of view that $\text{NiH}_2$ is formed compounds $\text{FeH}_2$ and $\text{FeH}_3$ (by the action of $\text{H}_2$ upon organic compounds of Fe).	Schlenk and Weichsefelder: <i>Ber.</i> , <b>56B</b> , 2330 (1923). Bredig and Allolio: <i>Z. phys. Chem.</i> , <b>126</b> , 41 (1927). Weichsefelder and Thiede: <i>Ann.</i> , <b>447</b> , 64 (1926).
Hydrogenation of benzene to cyclohexane.	Reduced Ni.		Active metal hydrides.	Sabatier and Senderens: <i>Compt. rend.</i> , <b>132</b> , 210 (1901).
Hydrogenation of benzene.	Ni.	The metallic catalysts effect rapid exchange of $\text{H}_2$ atoms between benzene and the gaseous hydrogen at ordinary temperature.	The hydrated oxide reduces more readily than any other form of oxide completely deprived of its combined water.	Ipatieff (confirmed by Sabatier and Aboulene): <i>Bull. Soc. Chim.</i> , <b>11</b> , 611 (1912).
Hydrogenation of benzene.	Ni.	$\text{H}_2 + \text{Ni}^* = \text{Ni}_2\text{H}_2$ $\text{Ni}_2\text{H}_2 + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_8 + 2\text{Ni}^*$	Active unstable hydrides in reduced Ni catalysts are divided into three classes: (1) most active are able to hydrogenate benzene and to be poisoned by thiophene; (2) can reduce ethylenic groups and be poisoned by ethyl sulfide; (3) able to reduce only nitro groups and are poisoned only by $\text{H}_2\text{S}$ .	Kubota and Joshikawa: <i>Sci. Papers Inst. Phys. Chem. Res.</i> , <b>3</b> , 223 (1925); <i>J. Phys. Chem.</i> , <b>1141</b> (August, 1927).
Hydrogenation of phenol.			Cyclohexanol, not benzene.	Roberti: <i>Ann. chim. applicata</i> , <b>21</b> , 217-221.
Catalytic reactions.	Metals.		Formation of unstable intermediate electronic complexes which decompose giving the final product of the reaction and regenerating the catalyst.	Job: <i>Deuxième Cons. Chim. Inst. Intern. Solvay</i> , 417 (1926).



Table 4 (Continued).

Reaction	Catalyst	Intermediate Reactions	Intermediate Compound	Observer
Variation in hydrogenation of oximes; acetaldoxime and propaldoxime are reduced exclusively to the corresponding tertiary amines; benzaldoxime yields a mixture of mono- and dibenzylamine, $\text{NH}_3$ and benzaldehyde; benzophenone oxime gives diphenylmethanamine; acetophenone oxime and dibenzylketoxime could not be reduced.	Colloidal Pd; Pd on $\text{BaSO}_4$ .	The formation of secondary and tertiary amines takes place through condensation of intermediary imines and aldehydes and reduction of condensation products.	Imines, aldehydes, condensation products of type $\text{R}-\text{CH}=\text{N}-\text{R}'$ and $\text{R}-\text{CH}=\text{N}-\text{CHR}-\text{N}=\text{CHR}$ .	Gulevitch: <i>Ber.</i> , 57B, 1645 (1924); <i>Chem. Soc.</i> 1283(f) (1924). Rossmund and Jordan: <i>Ber.</i> , 58, 51 (1925). Rossmund: <i>Z. ang. Chem.</i> , 38, 145 (1925). Rossmund and Pfankuch: <i>Ber.</i> , 56, 2259 (1923). Braude: <i>Ber.</i> , 57, 1652 (1924).
Homogeneous hydrogenation of cupri compounds and quinone; crotonic acid and azobenzene cannot be reduced under similar conditions with copper acetate compounds; the induction period in reduction depends on the aniline content of quinoline.	Cupro-acetate and cuprosalicyl-aldehyde in quinoline solution.		Copper-quinoline complexes assumed to be intermediate compounds.	Calvin: <i>Trans. Faraday Soc.</i> , 34, 1181-91 (1938).
Reversible dehydrogenation of hydroquinol.	Pt.		Pt acts as $\text{H}_2$ acceptor.	Manchot and Gall: <i>Der.</i> , 58, 486 (1925).
Dehydrogenation of thiophane to thiophene.	Pt on charcoal or NiS on alumina.	In both cases butadiene is postulated as an intermediate in a side reaction forming butene.	Dehydrothiophene.	Jurjew and Borisow: <i>Ber.</i> , 69, 1395-1398 (1936).
Dehydrogenation of ethyl alcohol to acetaldehyde.	Cu.	Five stages in the reaction: (1) ethyl alcohol in contact with copper; (2) intermediate complex formation; (3) redistribution of the intermediate complex; (4) desorption; (5) removal of acetaldehyde and hydrogen into the gaseous phase.	Intermediate complex: $\begin{array}{c} \text{CH}_3 \\   \\ \text{C}-\text{H} \\ / \quad \backslash \\ \text{H} \quad \text{O}-\text{H} \\   \quad   \\ \text{Cu} \quad \text{Cu} \\ \text{H}-\text{H} \\   \\ \text{Cu} \end{array}$	Frankenburger: <i>Z. anorg. Chem.</i> , 41, 531-562 (1928). Frankenburger and Dürr: "Katalyse," Urban and Schwarzenberg, Berlin, 1930. Frankenburger: <i>Z. Elektrochem.</i> , 39, 45, 97 (1933).

Table 5. Intermediate Compounds or Reactions in Catalytic Dehydration Reactions.

Reaction	Catalyst	Intermediate Reactions	Intermediate Compound	Observer
Dehydration of alcohol.	Alumina.	$\begin{aligned} &\text{AlO(OH)} + \text{C}_n\text{H}_{2n+1}\text{OH} \\ &\rightarrow \text{H}_2\text{O} + \text{AlO(O)} - \text{C}_n\text{H}_{2n+1} \\ &\text{AlO(O)} - \text{C}_n\text{H}_{2n+1} \\ &\rightarrow \text{C}_n\text{H}_{2n} + \text{AlO(OH)} \text{ or} \\ &2\text{AlO(O)} - \text{C}_n\text{H}_{2n+1} \\ &\rightarrow \text{C}_n\text{H}_{2n+1} - \text{O} - \text{C}_n\text{H}_{2n+1} + \text{H}_2\text{O} \end{aligned}$		Gregoriew: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>33</b> , 173 (1901). Ipatieff: <i>Ibid.</i> , <b>38</b> , 92 (1906). Ipatieff: "Catalytic Reactions at High Pressures and Temperatures," p. 541. The Macmillan Company, New York, 1936.
Dehydration of alcohol.	Alumina.	$\begin{aligned} &\text{Al}_2\text{O}_3 + \text{C}_2\text{H}_5\text{OH} \\ &\quad \text{O} - \text{C}_2\text{H}_5 \\ &\rightarrow \text{Al}_2\text{O}_2 - \text{OH} \end{aligned}$		Senderens: <i>Bull. soc. chim.</i> (4), <b>1</b> , 692 (1907).
Dehydration of $\text{C}_2\text{H}_5\text{OH}$ to 90-100% (olefin and little or no $\text{H}_2$ (340-350°).	$\text{ThO}_2$ , $\text{Al}_2\text{O}_3$ , $\text{W}_2\text{O}_5$ , $\text{Cr}_2\text{O}_3$ .	$\begin{aligned} &\text{ThO}_2 + 2\text{EtOH} = \text{ThO(OEt)}_2 + \text{H}_2\text{O} \\ &\text{ThO(OEt)}_2 = 2\text{C}_2\text{H}_5 + \text{ThO(OH)}_2 \\ &\text{ThO(OH)}_2 = \text{ThO}_2 + \text{H}_2\text{O} \end{aligned}$	Ethyl thorate or ethyl aluminate and other alkyl salts formed by the union of alcohol with the oxide which catalyzes the reaction.	Sabatier and Mailhe: <i>Ann.</i> , <b>20</b> , VIII, 289 (1910). Baskerville: <i>J. Am. Chem. Soc.</i> , <b>35</b> , 93 (1913). Senderens and Murat: <i>Ann. chim.</i> , <b>4</b> , IX, 283 (1913); <i>Compt. rend.</i> , <b>158</b> , 608 (1914). Senderens: <i>J. Ind. Chem.</i> , ... <b>681</b> , 702 (1927).
Dehydration of alcohols at high temperature.	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (dehydrated below 400°) and $\text{CaSO}_4$ (thoroughly calcined gypsum) or natural anhydrite).		Temporary hydrates.	Senderens: <i>Ann.</i> , <b>25</b> , 449 (1912).
Dehydration of alcohol.	Alumina, kaolin.		Aluminum ethylate, kaolin ethylate.	Sabatier: "Catalysis in Organic Chemistry," p. 240, 1914. Henderson: "Catalysis in Industrial Chemistry," p. 4, 1914.

Table 6. Intermediate Compounds or Reactions in Various Catalytic Processes.

Reaction	Catalyst	Intermediate Reactions	Intermediate Compound	Observer
Deacon's Process—chlorine.	Cu.	$4\text{CuCl}_2 = 2\text{CuCl}_2 + 2\text{Cl}_2$ $2\text{CuCl}_2 + \text{O}_2 = 2\text{CuO} \cdot \text{CuCl}_2$ $2\text{CuO} \cdot \text{CuCl}_2 + 4\text{HCl} = 4\text{CuCl}_2 + 2\text{H}_2\text{O}$ $4\text{CuCl}_2 + \text{O}_2 = 2\text{CuO} \cdot \text{CuCl}_2 + 2\text{Cl}_2$ $2\text{CuO} \cdot \text{CuCl}_2 + 4\text{HCl} = 4\text{CuCl}_2 + 2\text{H}_2\text{O}$	Either cuprous chloride, basic cupric chloride, or both, are the intermediate products.	Hurter: <i>J. Soc. Chem. Ind.</i> , <b>2</b> , 166 (1883). Bancroft: <i>J. Ind. Eng.</i> , <b>14</b> , 326 (1922).
Chlorination of benzene (1), toluene (2), xylenes (3); conversion of $\text{CS}_2$ to $\text{CCl}_4$ (4).	2–12% I.	$\text{ICl}_3 + \text{MH} = \text{HCl} + \text{MCl} + \text{ICl}$	$\text{ICl}_3$ could be isolated.	(1) Müller: <i>J. Chem. Soc.</i> , <b>15</b> , 41 (1862); Jungfleisch: <i>Ann. Chem. Phys.</i> (4), <b>15</b> , 186 (1868). (2) Hubbard and Mayest: <i>Ber.</i> , <b>6</b> , 190 (1893). (3) Koch: <i>Ber.</i> , <b>23</b> , 2319 (1890). (4) Helfrich and Reid: <i>J. Am. Chem. Soc.</i> , <b>43</b> , 593 (1921); E. P. 18,890, 1899.
Reaction of benzoyl chloride yielding an addition compound of the ketone.	$\text{SbCl}_5$ .		First an addition compound is formed between the hydrocarbon and the catalyst $2\text{SbCl}_5 \cdot \text{C}_6\text{H}_5\text{R}$ which then reacts with the acyl chloride.	Menshutkin: <i>J. Chem. Soc. (Abstracts)</i> , <b>i</b> , 188, 673 (1914).
Reaction between p-bromobenzene-sulfonyl chloride, $\text{C}_6\text{H}_4\text{BrSO}_2\text{Cl}$ and $\text{C}_6\text{H}_6$ .	$\text{AlCl}_3$ .	In certain cases the acyl chloride may form an addition compound with the hydrocarbon, i.e., $\text{CH}_3\text{COCl}$ with hexene yields 2-chlorocyclohexylmethylketone and this, by giving off $\text{HCl}$ , results in tetrahydroacetophenone.	The acyl chloride reacts solely in the form of the addition compound with $\text{AlCl}_3$ .	Olivier: <i>Rec. trav. Chim. Pays-Bas</i> , <b>33</b> , 91 (1914). Rubidge and Qua: <i>J. Am. Chem. Soc.</i> , <b>36</b> , 732 (1914). Wieland and Battag: <i>Ber.</i> , <b>55</b> , 2246 (1922).

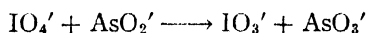
Polymerization of olefins, such as propylene and butylene into higher polymers (200° under pressure).	Liquid $\text{H}_3\text{PO}_4$ .	$2(\text{CH}_3)_2\text{C}=\text{CHO} \cdot \text{PO}(\text{OH})_2 = \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{CH}(\text{CH}_3)_2 + 2\text{PO}(\text{OH})_2$	Phosphoric acid monopropyl ester; through the addition of the ester, polymers are formed.	Isotaffel: <i>Ind. Eng. Chem.</i> , <b>27</b> , 1067-1069 (1935).
Polymerization of acetylene.	Aqueous solution (18% $\text{CuCl}$ + 20% $\text{NH}_4\text{Cl}$ ) (room temperature).		$6\text{CuCl} \cdot 3\text{NH}_4\text{Cl} \cdot \text{C}_2\text{H}_2$ (yellow crys. ppt.); in vacuum and by increased temperature the intermediate empd. dissociates giving off acetylene and decolorizing.	Zurich and Ginsburg: <i>Zh. obshchei. Khimii</i> , <b>5</b> (67), 1468-1478 (1935).
Formation of acetone from acetic acid.	$\text{BaCO}_3$ , $\text{CaCO}_3$ .	$2\text{CH}_3\text{CO}_2\text{H} + \text{CaCO}_3 = \text{CH}_3\text{CO}_2\text{Ca} + \text{H}_2\text{O} + (\text{CH}_3\text{CO}_2)_2\text{Ca}$ ( $\text{CH}_3\text{CO}_2\text{Ca} = \text{CaCO}_3 + \text{CH}_3\text{COCH}_3$ )	Barium or calcium acetate considered as an intermediate product.	Squibb: <i>J. Am. Chem. Soc.</i> , <b>17</b> , 187 (1895).
Hydrolytic reactions.	$\frac{1}{2}$ mol $\text{HCl}/1$ .	$\text{CH}_3\text{R} - \text{C}(=\text{O}) + \text{H}^+ \rightarrow \text{CH}_3\text{R} - \overset{+}{\text{C}}(\text{OH})(\text{H}^+)$ $\text{CH}_3\text{R} - \overset{+}{\text{C}}(\text{OH})(\text{H}^+) \rightarrow \text{CH}_3\text{R} - \text{C}=\text{O} + \text{H}^+$ $\text{CH}_3\text{R} - \overset{+}{\text{C}}(\text{OH})(\text{H}^+) \rightarrow \text{H}^+ + \text{CHR} = \overset{+}{\text{C}}(\text{OH})(\text{H}^+)$	A salt is formed between the catalyst and the reacting substances.	Euler, Olander and Rudberg: <i>Z. anorg. ang. Chem.</i> , <b>146</b> , 45 (1925).
Conversion of the keto into the enol form (phenyl- $\alpha$ -alkyl ketone in 0.1 molar solution of 75% acetic acid).			Oxonium ion (activated intermediate compound); an exchange action between the unpaired electrons of the carbonyl oxygen and the covalent hydrogen.	Evans: <i>J. Chem. Soc. (London)</i> , 785-789 (June, 1936).
(1) Iodide ion catalysis of periodate-arsenite and (2) Iodide ion catalysis of $\text{H}_2\text{O}$ -thiosulfate.	Iodide ion.	$\text{IO}_3' + \text{AsO}_3' \rightarrow \text{IO}_2 + \text{AsO}_2$		Abel: <i>Rec. trav. Chim. Pays-Bas.</i> , <b>41</b> (4), 610 (1922).

hydrogenation reactions, metallic hydrides have been considered to be the intermediate compounds in many cases. Salts, such as barium or calcium acetate, have been claimed as the intermediates in the conversion of acetic acid to acetone in the presence of the carbonates of the metals; and ester formation was believed to play an important role in the conversion of alcohols to olefins by the action of alumina or thoria, or to amines or thiols in the presence of ammonia or hydrogen sulfide. In some cases it is questionable whether the intermediates are true compounds. The hydrides of nickel ( $\text{NiH}_2$ ,  $\text{NiH}_4$ ), iron ( $\text{FeH}_2$ ,  $\text{FeH}_6$ ), platinum, or palladium ( $\text{Pd}_3\text{H}_2$ ), for example, may not contain chemical bonds such as are involved in the alkali metal hydrides, but may contain hydrogen loosely held or occluded on the metal surface.

Although, as in the case of ethyl sulfuric acid in ether formation, or alkyl phosphates in olefin polymerization, an isolated intermediate has been shown to play an actual part in the investigated reaction, it is now generally recognized that the isolation of a compound which decomposes to the correct end-products furnishes no proof that such an intermediate takes part in the original reaction, especially when the experimental conditions must be altered to effect the isolation.

### Kinetics of Reactions Involving Intermediate Compounds

It was the belief of those who subscribed to the intermediate compound theory that the chief problem of chemical kinetics in catalytic reactions would be solved if it were possible to calculate in advance the reaction velocity of a catalytic system from the concentrations and from individual constants of the catalyst and the reacting substance. The iodide ion catalysis of the hydrogen peroxide-thiosulfate reaction has been considered as an example of catalysis in which the velocities of the non-catalyzed (direct), the catalyzing and the catalyzed reaction may be determined separately. The iodide ion catalysis in the periodate-arsenic acid system furnished another example in which the conception of intermediate reactions is confirmed by a measurable increase in the reaction velocity quantitatively predictable.<sup>1</sup> The catalytic reaction between periodate and arsenic acid by iodide ion proceeds as follows:



The reaction, which is bimolecular, may be expressed by the equation:

$$V = \frac{dC}{dt} = \frac{d(\text{IO}_4')}{dt} = K(\text{IO}_4')(\text{AsO}_2')$$

in which  $K$  is the velocity constant. The reduction of periodate to iodate by means of the iodide ion catalyst occurs practically quantitatively for a definite hydrogen ion concentration and without further reduction of the iodate formed. The time necessary for the reaction to occur is a function of the transformation occurring and may be calculated from the equation:

$$t = \frac{2 \cdot 303}{K_1C - K_2(a-b)} \frac{\log K_1aC}{(a-b)(K_1C + K_2b)}$$

where  $a$  and  $b$  denote the initial concentration of the periodate and arsenic acid;  $C$ , the concentration of the catalyst—iodine ion;  $K_2$ , the velocity constant of the non-catalyzed direct reaction, and  $K_1$ , the velocity constant of the catalyzing reaction.

The idea of the simultaneous formation of several catalytically active intermediate products was introduced by Spitalsky who studied the catalysis of hydrogen peroxide decomposition with molybdenum. According to Spitalsky's conceptions, the catalyst converts the reacting substance into a state in which it becomes capable of reacting by the formation of labile intermediate compounds. Proceeding as a reversible process, the formation of the intermediate compound is relatively instantaneous. The degree of affinity of the catalyst for the reacting substance is expressed by the equilibrium constant for the process. The velocity of the complete catalytic reaction is proportional to the concentration of the intermediate compounds, but not to that of the reacting substance, and is equal to the sum of the decomposition velocities of single intermediate compounds. If ions, especially  $H^+$  and  $OH^-$ , participate in the formation of intermediate compounds, their concentration must also be considered in the evaluation of the concentration of the intermediate compounds.

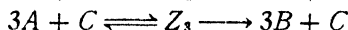
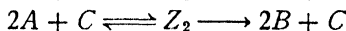
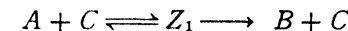
In the case of the molybdenum-catalyzed decomposition of hydrogen peroxide, Spitalsky assumed two intermediate products characterized by different affinity constants and degrees of lability. The velocity of catalysis was considered to be proportional to the concentration of the dominating intermediate product and dependent on the acidity or alkalinity of the solution. In weak acid, as well as in weak alkali solutions, the velocity of catalysis was found to be constant and independent of the concentration of hydrogen peroxide; such kinetics indicate the instantaneous formation of at least one intermediate product.

Chemical kinetics is based on the assumption that the kinetic equation is of an *integral* order. In the attempt to confirm the mechanism of intermediate compound formation by kinetic laws, it was ascertained that the order of a catalytic reaction varies with the action of different catalysts,<sup>24</sup> and that in many cases the kinetic course of the reaction deviates from an integral order. To correlate these facts, Spitalsky<sup>88</sup> differentiated two conceptions of the reaction order: (1) a "chemical reaction order," and (2) a "kinetic reaction order." The "chemical reaction order" expresses the number of molecules of the reacting substance entering into a chemical reaction with the catalyst and corresponds to an integral order, while the "kinetic reaction order" is derived from the kinetic equation of the velocity curve. If the chemical reaction order is  $n$ , then the catalytic reaction may proceed by an optional kinetic order, depending upon the magnitude of the affinity constant, the latter being expressed by the formula:

$$K = \frac{T_2 \ln \frac{C_1}{C_2} - T_1 \ln \frac{C_3}{C_4}}{T_1(C_3 - C_4) - T_2(C_1 - C_2)}$$

where  $t_2 - t_1 = T_1$  and  $t_4 - t_3 = T_2$  indicate time intervals, and  $C_1, C_2,$

$C_3$  and  $C_4$  denote concentration of the reacting substance; the mechanism of the reaction is as follows:



$$K_1 = \frac{[Z_1]}{[A][C]}$$

$$K_2 = \frac{[Z_2]}{[A]^2[C]}$$

$$K_3 = \frac{[Z_3]}{[A]^3[C]}$$

$K_1$  rate constant for decomposition of  $Z_1$  etc.

The kinetic course of a catalytic reaction in which three reversible intermediate products are formed simultaneously between a molecule of the catalyst and one, two, or three molecules of the reacting substance, is expressed by the equation:<sup>91</sup>

$$V = \frac{dC}{dt} = \frac{CF(k_1K_1C_s + k_2K_2C_s^2 + k_3K_3C_s^3)}{1 + K_1C_s + K_2C_s^2 + K_3C_s^3}$$

where  $C_s$  is the concentration of the reacting substance. Thus the resulting velocity of a catalytic reaction is proportional to the concentration of the reacting substances and is equal to the sum of decomposition velocities of single intermediate compounds.

These formulae were believed to be instrumental in calculating in advance the reaction velocity of a catalytic system from the concentrations and the individual constants for the catalyst and the reacting substances. Since a catalyst is essentially an agent for the more rapid attainment of the equilibrium state between the reacting and the resulting components, it has been assumed that any theory of catalysis must conform with the laws of chemical thermodynamics. As the equilibrium constant is the ratio of the two velocity constants for mutually reversible reactions, a catalyst which accelerates one reaction must therefore also accelerate the reverse one; otherwise the equilibrium constant would change its value at the given temperature, making possible a perpetual motion of the second kind, contrary to the second law of thermodynamics.

The relationship between the equilibrium constant and the temperature  $T$  is usually expressed by the equation:

$$\frac{d \ln K}{dT} = \frac{Q}{RT^2}$$

When integrated, the equation becomes:

$$K = Ce^{-Q/RT}$$

Chemical kinetics shows that the velocity constants ( $K_1$  and  $K_2$ ) of mutually reversible reactions are:

$$K_1 = C_1 e^{-q_1/RT}$$

$$K_2 = C_2 e^{-q_2/RT}$$

The forward velocity of the reaction  $V_1$  is proportional to the number of collisions between  $m$  molecules of substance  $A$  and  $n$  molecules of substance  $B$ ,  $V_1 = K_1(A)^m(B)^n$  and likewise for the velocity  $V_2$  of the reverse reaction the equation  $V_2 = K_2(C)^u(D)^p$  is obtained. The equilibrium state requires that

$$V_1 = V_2, \text{ or } K_1(A)^m(B)^n = K_2(C)^u(D)^p, \text{ or } \frac{K_2}{K_1} = K, \text{ or } \frac{K_2}{K_1} = K = Ce^{-Q/RT}.$$

This means that if, in a catalytic reaction,  $C_1$  or  $q_1$  changes, then  $C_2$  and  $q_2$  change in such a manner that  $C$  and  $Q$  remain unchanged.  $C_1$  and  $q_1$ , therefore, essentially describe the catalytic action. In the expression  $C_1e^{-q_1/RT}$ , representing the velocity constant of the reaction, increases at a given temperature are brought about either by increasing  $C_1$  or by decreasing  $q_1$ . The increase of  $C_1$  corresponds to an increase in velocity caused by the increase in the number of collisions of molecules in the system. The number of collisions is proportional to the velocity of the molecules, which is proportional to the square root of the absolute temperature ( $T$ ). Thus one would expect that the increase of  $T$  by  $10^\circ$  (at initial room temperature) would increase the reaction velocity by 2 per cent; but it is known that in some reactions the velocity increases two or three times. On the other hand, the equilibrium constant would be the same for reactions with equal coefficient values in the chemical equation ( $m$ ,  $n$  and  $u$ ,  $p$ ) and all reactions would proceed rapidly if every collision of the corresponding molecules caused reaction. Actually, the equilibrium constants and velocity constants are very specific for each reaction. Not all collisions lead to reaction and not all molecules behave alike; some are more active than others. The conception that molecules are differentiated by their state of activation, as well as by their velocity, limits the importance of the collision factor  $C$  in determining the final reaction velocity and in evaluating the catalytic action. A catalyst not only increases the "mechanical" factor of collisions  $C$  whereby a considerable number of collisions lead to the formation first of intermediate and second of final products, but the catalyst also affects the factor of activity  $q_1$ . The value of  $q_1$ , entering the second member of the above equation and characteristic for each kind of molecule, as well as for each reaction, expresses the minimum or threshold of energy which a molecule must have in order to react. If in a chemical reaction the energy  $q_1$  should decrease, then the fraction  $e^{-q_1/RT}$  would increase, *i.e.*, a greater number of molecules would become active. The reaction is, therefore, accelerated when the threshold of energy decreases. This will take place (but not necessarily) when intermediate products are formed if their energy  $q_1$  is smaller than the energy  $q$  characteristic of the direct reaction.

### Dislocating or Disruptive Action of the Catalyst

The ease of formation of labile intermediate products may assist in accelerating a reaction but other factors, such as molecular resonance and deformation of electronic orbits in molecules caused by the catalyst, may be just as effective in the activation of a greater number of molecules.



When a catalytic reaction takes place, a certain intermediate state of reacting components, different from their initial state, seems to exist. The reacting substances are brought into an intermediate state which is the result of intramolecular processes caused by the catalyst or changes of bonds between the reacting substance and the catalyst. In either case, an increased activity in the system results. A series of transition steps is postulated as existing between the initial and the final state of stability. Assuming that a stable state is characterized by a definite order within the molecule and definite orbits and moments of inertia, the intramolecular ionization or predissociation manifests itself by weakening the intramolecular bonds or by decreasing the compact state of the molecule. The latter result is evidenced by a change of the moment of inertia, an increase in size, and an elongation in the diameter of the molecules.

It is believed that a "dislocating" or a "disruptive" action<sup>18</sup> upon activated molecules may be provoked by a mere physical contact between the catalyst and the reacting components of the system. The catalyst, without combining intimately at the position of the bond which it must activate, changes the trajectories of electrons in a manner so that the molecules of reacting substances may act more rapidly than without this change, which Boeseken refers to as "dislocation." It is postulated that this "dislocation" occurs with high speed. A good catalyst ought not to form stable addition complexes, but ought to enter into an equilibrium with the activated molecules which is shifted as far as possible toward the formation of free molecules. The best catalysts are those which exert neither weak nor strong influence on the reactants over an extensive interval of temperature and pressure; a too-intimate union of the catalyst with the reactant is undesirable.

The dislocating action of a catalyst is believed to be electrical in nature. Powerful catalysts, substances such as sulfuric acid, aluminum chloride, ferric chloride, which ionize readily or have residual valences have been classified as "open systems," while the reacting organic molecules, even those that are unsaturated, belong to "closed systems." When these two systems approach each other, the catalyst extends its own open and polar character upon the less polar molecules of the reactants, leaving them in a state of greater polarity and higher activity. It is reasonable to assume that a polar molecule will change another molecule into a state of greater rather than lesser polarity.

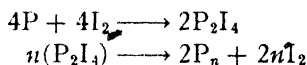
The following types of an ordinary catalysis were postulated by Boeseken: (1) a substance is formed through activation by an external source of energy through the agency of the catalyst; (2) the combination of the catalyst with the molecules it activates establishes a favorable orientation which makes possible the change in the characteristic trajectories of electrons; (3) the catalyst induces the conversion of closed bonds into open ones, so that a higher reaction velocity is effected, this being the catalyst function in the dislocation or disruptive action; and (4) the dislocation of special bonds may indicate the place where the molecules have been activated. Since, for example, the anhydride of acetic acid forms acetyl sulfuric acid with sulfuric acid, it is probable that the dislocation of the an-

hydride by sulfuric acid occurs at the bond  $\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array}$  when the acid is used

as an acetylation catalyst. The dislocated anhydride may then attack an alcohol or a phenol the O-H bond of which is also dislocated by sulfuric

acid. When the compound  $\text{CH}_3\text{---}\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array} \text{---}\text{SO}_2\text{---}\text{OH}$  is once formed the

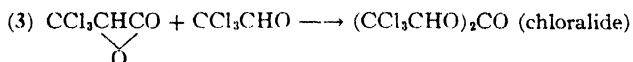
catalytic effect disappears. The dislocation of special bonds occurs during the first contact when the catalytic reaction actually takes place. In case of a bimolecular reaction, the dislocated bond may act more rapidly upon the bond of another molecule which, under similar conditions, has already undergone a change due to the catalyst. Thus a simultaneous dislocation of two molecules takes place in which the dislocation of one of the molecules depends not only on the catalyst, but also on the nature of the other molecule. It is further assumed that in some cases the catalyst simultaneously dislocates both molecules. In the case of polymolecular systems, the accelerating action of the catalyst was believed to direct the specific bonds, that is, to dislocate them toward one another into a particular orientation. Boeseken illustrated the significance of the dislocation action by allotropic transformation of one element under the catalytic action of another element:



The same reaction occurs when phosphorus tribromide is used, but the catalytic action with bromine proceeds at a much higher temperature than in the case of iodine. The conversion of white phosphorus into red in the presence of aluminum chloride was interpreted similarly. The conversion of chloral by the action of pyridine, sulfuric acid, or aluminum chloride,<sup>19</sup> is another example of dislocation action, but one in which the latter is partially substituted by dissociation. The primary reaction is disruption of chloral into two parts, the dislocation occurring at the same place as the subsequent scission. When the molecule of chloral decomposes, the reaction proceeds as follows:

- (1)  $\text{CCl}_3\text{CHO} \longrightarrow \text{CCl}_2 + \text{HCICO}$  (formyl chloride)
- (2)  $\text{CCl}_3\text{CHO} + \text{HCICO} \longrightarrow \text{CCl}_2\text{CHCO} + \text{HCl} \longrightarrow \alpha \text{ lactide of chloracetic acid}$

and this condenses with a third molecule of chloral to form chloralide:



The molecular fragment  $\text{CCl}_2$ , in the presence of sulfuric acid, reacts with sulfur trioxide to form phosgene:



Various catalysts may bring the same molecule into different states of dislocation, the newly established equilibrium depending on the nature of the activator. According to Boeseken, sulfuric acid and zinc chloride act upon the unsaturated oxygen of an aldehyde activating the formation of paraldehyde, while bases exert a dislocating action upon one of the hydrogen atoms accelerating the formation of aldol.

### Energy Factor in Catalysis

According to Boeseken, the dislocation action is a change of energy, and catalysis corresponds to a dislocation of fields of forces in a metastable system caused by the interaction of the fields of forces of the catalyst with that of activated bonds.

From a thermodynamic point of view, the possibility of any chemical reaction and that of the intermediate state through which molecules have to pass in order to be able to react is determined by two values, namely, the energy and the entropy. The efficiency of a catalyst in altering the chemical reaction itself or the intermediate state through which it passes, is consequently also limited by changes in these values. The enormous acceleration of almost all reactions on increase in temperature<sup>5</sup> cannot be accounted for simply by the increase of the total number of collisions of molecules; only few of them receive violent impulses bringing about an internal energy sufficient for the reaction. The influence of temperature upon the reaction depends not only upon the number of collisions, but also is a function of the kind of collisions.<sup>44</sup> Whether molecules will react with one another depends upon the direction of the collision in addition to its force.

The relationship between the velocity constant and the temperature, according to Arrhenius, is:

$$\ln K = \frac{-A}{RT} + B$$

In this equation  $A$  denotes the difference in energy between that of active molecules and the average energy of the whole mass. The quantity  $A$  is regarded as the activation energy, but  $B$  remained undefined until Scheffer and Kohnstamm<sup>79</sup> introduced the conception that molecules, in order to react, have to pass through an intermediate state characterized by a definite difference in entropy with regard to the average, as well as by a definite difference in the energy compared with its average. The value of  $B$  received a more definite meaning through the following formula of Arrhenius-Scheffer and Kohnstamm:

$$\ln K = \frac{-\epsilon_i - \epsilon_m}{RT} + \frac{\eta_i - \eta_m}{K} + C$$

in which  $\epsilon_i - \epsilon_m$  and  $\eta_i - \eta_m$  at unit concentration represent differences in energy and entropy, respectively, for the intermediate state and the total mass. They assumed that the energy and the entropy of the intermediate state are both altered by the catalyst, both the reacting molecules and the

catalyst being present in the intermediate state. Thus in catalysis of an isomeric change two cases may be differentiated:

$$(1) \ln K = \frac{-\epsilon_i - \epsilon_m}{RT} + \frac{\eta_i - \eta_m}{K} + C \text{ without a catalyst}$$

$$(2) \ln K = \frac{-\epsilon_i - \epsilon_m - \epsilon_{cat.}}{RT} + \frac{\eta_i - \eta_m - \eta_{cat.}}{K} + C' \text{ with a catalyst}$$

where  $\epsilon_i - \epsilon_m$  is the difference between the average energy of active molecules (in the intermediate state) and that of the total mass; and  $\eta_i - \eta_m$  is the difference in entropies calculated for unit concentration of the total mass. The first term is that of the activation energy or the "critical" energy; the second is a calculable term characteristic of the mechanism of the reaction and as a rule depending largely on the velocity.

The energetic course of a catalytic reaction in which intermediate products are formed has been related to their formation *in statu nascendi*.<sup>41, 42</sup> As derived from the above equations it follows that when the catalyst forms intermediate chemical compounds a decrease in the activation energy and a rather small change in the entropy are involved. The dislocating action of the catalyst manifests itself in a small change in the activation energy and is due to the difference in the entropy value.

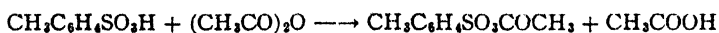
From the viewpoint of energy relations, Boeseken deduced the possibility of three types of catalysis. In physical catalysis the term  $A$  of the Arrhenius equation varies but little and the change in velocity is governed by an increase in the  $B$  term; in chemical catalysis the term  $A$  changes noticeably, either in a positive or a negative sense. The group of catalytic reactions in which the addition of a catalyst does not change the activation energy and consequently the effect of a catalyst must be attributed entirely to the variation of term  $B$  Boeseken defined as "ideal" catalysis. In general, as indicated by experimental evidence, catalysts change both values,  $A$  and  $B$ , and the "ideal" catalysis may be referred to as a limiting case asymptotically approached by true catalytic phenomena.

Physical, chemical and "ideal" catalyses were demonstrated<sup>98, 18</sup> in acetylation with acetic anhydride and the catalysts *p*-bromo- and *p*-methyl-phenyl sulfonic acids, which exert physical forces upon each other because of the great mutual "affinity" of anhydrides and strong acids. A paralysis of the catalyst would be expected under conditions which increased the activation energy, but this would lead to a slowing down of the reaction if the term

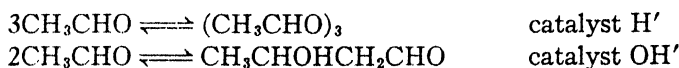
$$\frac{\eta_i - \eta_m}{K} \quad (C = 1)$$

did not increase greatly.

The formation of a new molecule, an intermediate product, namely, the anhydride of paratolysulfo-acetate, was also considered possible in this example. The catalytic reaction would be as follows:



As an example of an almost "ideal" catalysis, the equilibrium states of simple molecules undergoing changes such as polymerization are discussed.<sup>18</sup> For example, acetaldehyde may be converted into paraldehyde or aldol:



The equations for the velocity of polymerization (concentration = 1), the concentration of catalysts being included in constants  $K$  and  $K'$ , are as follows:

$$\begin{aligned} \ln K &= \frac{-\epsilon_i - 3\epsilon_A - \epsilon_{\text{cat.1}}}{RT} + \frac{\eta_i - 3\eta_A - \eta_{\text{cat.1}}}{K} + C_1 \\ \ln K' &= \frac{-\epsilon_i - 2\epsilon_A - \epsilon_{\text{cat.2}}}{RT} + \frac{\eta_i - 2\eta_A - \eta_{\text{cat.2}}}{K} + C_2 \end{aligned}$$

The critical state of the aldehyde is altogether different in the two cases; the velocity of these reactions must be measured at different temperatures. The critical states of paraldehyde and aldol molecules correspond to those of the aldehyde in different states of activation.

As has been pointed out previously, Boeseken's "dislocation" hypothesis regards "physical" catalysis as a purely dislocating action, the catalyst causing acceleration without an appreciable loss in energy. The changes which are called dislocations are determined exclusively by the increase of the term  $B$  in Arrhenius' equation. The "chemical" catalysis or catalysis of intermediate compounds may operate by the same dislocating forces active in "physical" catalysis, but the formation of a combination more or less stable between the catalyst and the reacting molecules involves an increase of the term  $A$  (called by Boeseken an "energy paralysis" of the catalyst), and this is more than counterbalanced by an increase of the term  $B$ . If the terms  $\epsilon_i$  and  $\epsilon_{\text{cat.}}$  are almost equal, then the differences in velocity must be attributed largely to the difference in value of the terms  $\eta_i$  and  $\eta_{\text{cat.}}$ . Boeseken illustrated this relationship by the conversion of chloral into metachloral using as catalyst either sulfuric acid or pyridine, the intermediate compounds of which are rather stable at ordinary temperature. If it is admitted that the formation of intermediate compounds causes a notable variation in the activation energy while physical catalysis produces only small changes, then it follows that temperature will have quite a significant influence upon the value of the apparent activation energy, for intermediate products dissociate under heating, and at elevated temperature the mechanism of consecutive reactions is replaced by a direct conversion. At low temperatures there is more or less deviation from the Guldberg and Waage formula; at moderate temperatures, direct and indirect conversions occur simultaneously; while at high temperatures the direct reactions become more predominant. Therefore, a remarkable deviation from the Arrhenius formula is observed. The activation energy calculated from the Arrhenius equation decreases with increase in temperature. Arrhenius assumed that a positive catalyst makes the difference of energy

A smaller and, consequently,  $\ln K$  becomes greater. This supposition, in connection with the original formula of Arrhenius:

$$\frac{d \ln k}{dT} = \frac{A}{RT^2}$$

makes it necessary that the temperature coefficient in the presence of a catalyst always be smaller than in the absence of a catalyst. To put the matter another way, if the velocity is regulated by the number of active molecules

$$e^{-E/RT}$$

and if a positive catalyst always decreases the increment of energy  $\epsilon$ , then the temperature coefficient must be decreased in the presence of a catalyst. This temperature coefficient, however, was found experimentally to be greater for the catalytic reaction<sup>98</sup> than for the non-catalytic. On the other hand, Scheffer and Brandsma,<sup>78</sup> who assumed that a catalytic reaction occurs independently of the reaction itself, drew attention to the fact that in an intermediate state of the primary action the catalyst is also present and, consequently,  $\epsilon_i$  and  $\eta_i$  are not the same in both cases. Therefore either an increase or a decrease in the energy increment may be expected, and there is no way at present of predicting the influence of the catalyst upon the activation entropy.

### Increase in Absorbable Radiation through Catalysis

In the short time that molecules of reacting substances are under the influence of a catalyst, the forces acting between atoms or molecules are quickly changed, acquiring a greater activity. This change in activity is assumed to be induced by energy absorbed by the catalyst. This energy may be minute in comparison with the amount of matter converted by it into the active state. Planck's theory emphasizing the necessity of an addition of energy in terms of quanta of an absorbable type was considered applicable to thermal as well as catalytic reactions. The effect of radioactive rays in assisting chemical reactions was at first compared with catalysis but later was differentiated from this type of reaction. It was emphasized<sup>51</sup> that in catalytic reactions no definite relationship exists between the amount of electrical or kinetic energy involved and the resulting yield of the reaction as is the case for chemical reactions assisted by radioactive rays. Catalysts usually act in solutions somewhat in proportion to their concentration, whereas radioactive substances do not.

In 1906 Trautz suggested that ordinary chemical reactivity is restricted to the infrared region because at ordinary temperature the greater part of the radiation present in a system is of the infrared type. Trautz and Krüger<sup>102</sup> postulated that radiation is the source of energy which makes chemical reactivity possible. A quantitative relationship was developed between the reactivity of various molecular species in a reacting system and the radiation density in terms of the quantum theory. The reaction velocity of a system was formulated as:

$$\frac{dx}{dt} = \alpha e^{-E/RT}$$

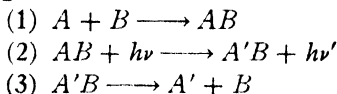
where  $\alpha$  denotes an arbitrary constant and  $E$  the "critical" energy increment which, when contributed to a gram molecule of the substance, converts it from the ordinary into the reactive state. The quantum theory gives a method for estimating quantitatively the energy required for the removal of an electron from the atom or forcing it into a new orbit. The activation of a molecule proceeds in stages and with definite energy increments corresponding to various oscillation frequencies of the valence electrons until one or more of them leave the atom and a complete ionization is brought about.

The velocity constant and the temperature factor were correlated<sup>54</sup> in the expression:

$$\frac{d \ln K}{dT} = \frac{E}{RT^2}$$

This expression was derived by the methods of statistical mechanics with the assumption that a molecule reacts only when its internal energy has been raised to a certain "critical" value, the term  $E$  denoting the difference between this critical energy and the average molal internal energy. The interchange between the matter and the radiant energy is supposed to be effected through the medium of oscillators placed on the molecules present in the system.

Perrin<sup>63</sup> proposed a theory of catalysis which assumed that chemical reactions are brought about by photochemical radiations through the influence of the catalyst. The reacting substance, when it absorbs a high frequency radiation, is converted to the product with the evolution of radiation of another frequency. With reference to catalysis, this is expressed in the following scheme:



where  $A$  is the reactant,  $B$  the catalyst,  $\nu$  the absorbed frequency,  $\nu'$  the emitted frequency, and  $A'$  the reaction product.

On the basis of the quantum theory Lewis, in a series of papers,<sup>49</sup> discussed the reactivity of substances participating in catalysis. Since Guldberg and Waage, the concentration of a substance has been regarded as an accurate measure of the active mass (except when there is association, dissociation, hydration and tautomerization, etc.), but when the energy exchanges preceding molecular changes in the system were taken into account, this viewpoint had to be modified and the active mass considered to be dependent on the radiational environment. The increase in radiation density contributing to the reactivity of components in a catalytic reaction was assumed to be a product of two factors: (1) the active mass, identified with the number of molecules brought into an active state due to the radiation, and (2) the radiational environment or radiation density. On the basis of Planck's quantum theory, the radiation density is expressed as:

$$U_\nu = \frac{8\pi h \nu^3 n^3}{C^3} \cdot \frac{1}{e^{Nh\nu/RT} - 1}$$

where  $h$  is Planck's constant,  $h\nu$  the quantum of radiant energy corresponding to the frequency  $\nu$ ,  $n$  the refractive index of the system for the region containing frequency  $\nu$ ,  $c$  the velocity of light in a vacuum,  $R$  the gas constant per gram molecule,  $N$  the number of molecules in a gram molecule, and  $T$  the absolute temperature.

As previously assumed, the region of chemical reactivity is that of the short infrared; thus values of  $\nu$  are such that

$$e^{N h \nu / R T} - 1$$

approximates the value of

$$e^{N h \nu / R T}$$

and a more simple form of the above expression is obtained:

$$U\nu = \frac{8\pi h \nu^3 n^3}{C^3} \cdot e^{-h \nu N / R T}$$

If the radiation density has too small a value, then the substance will not react in spite of a high concentration.

According to Lewis' "radiation hypothesis"<sup>45a, 48a, 72a, 95</sup> interpretation of the mechanism of catalysis, the function of a positive catalyst is to increase the radiation density of the absorbable type of radiation so that a greater number of molecules of the reactants attain a "critical" value for their internal energy resulting in an increase of the reaction velocity. Regarding the influence of temperature and catalysts upon the rate of the reaction, Lewis therefore concluded that the active mass which determines the rate is proportional to the concentrations of both the reactants and the catalyst, as well as to the radiation density, which is a function of the temperature. Lewis considered in this connection only homogeneous catalysis.

If  $a$  is the initial concentration of the reactant and  $x$  the amount converted in time  $t$ , then the velocity is expressed by:

$$\frac{dx}{dt} = \alpha C_s(a-x) U\nu \alpha \cdot C_s(a-x) \frac{8\pi h \nu^3 n^3}{C^3} \cdot e^{-h \nu N / R T}$$

where  $\frac{8\pi h \nu^3}{C^3}$ ,  $C_s$ , the catalyst concentration, and  $n$  are regarded as constants throughout the course of the reaction.

Thus  $\frac{dx}{dt} = P(a-x)n^3C_s e^{-h \nu N / R T}$  which at constant temperature is identical with the ordinary mass action equation. On integration this becomes

$$\frac{1}{t} \ln \frac{a}{a-x} = k = P C_s n^3 e^{-h \nu N / R T}$$

Differentiating this equation with respect to temperature, and correcting for the variation of the refractive index  $n$  with catalyst concentration and temperature, Lewis obtained finally the equation

$$\frac{d \ln k}{dT} = \frac{N h \nu - \frac{3(b + \gamma C_s) R T^2}{n_1}}{R T^2}$$



where  $N$  is Avogadro's number;  $h$ , Planck's constant;  $b$ , a constant depending on the solvent;  $\gamma$ , a constant depending on the catalyst (positive for a positive catalyst, negative for a negative catalyst, and zero in the absence of a catalyst);  $C_c$ , the concentration of the catalyst, and  $n\nu$ , a function of  $n$ , the refractive index of the system for the region containing the frequency  $\nu$ . From this equation it follows that a positive catalyst which increases the reaction velocity decreases the temperature coefficient, while a negative catalyst which decreases the reaction velocity increases the value of the temperature coefficient. In other words, from the quantum radiation viewpoint of chemical reactivity, it has been deduced that the value of the temperature coefficient is a function of the presence of either a positive or a negative catalyst.

The influence of temperature on the specific reaction velocity found its expression also in other formulas. Banerji and Dhar<sup>6</sup> proposed

$$K = Se^{-Q/RT}$$

where  $K$  denotes the specific velocity of the reaction;  $S$ , a constant with frequency dimensions, and  $Q$ , the energy. Lewis<sup>49</sup> and Perrin<sup>63</sup> considered  $Q$  as the radiation energy  $h\nu$  of the activating frequency  $\nu$  which must be absorbed to enable a molecule to react. In other words, Lewis' suggestion was that  $K = n^3 p e^{-Q/RT}$  in which  $p = \frac{8\pi h\nu^3}{C^3}$ , where  $C$  denotes the velocity of light in a vacuum and  $n$  the refractive index of the system with a frequency  $\nu$ . Lewis and McKeown<sup>49</sup> proposed the equation:

$$K = 2.465 \cdot 10^{-22} n^3 \nu^3 e^{-h\nu N/RT}$$

Tolman<sup>101</sup> believed that Dushman's equations fit best, namely,

$$K = \frac{Q_A}{Nh} \cdot e^{-Q_A/RT}$$

where  $Q_A$  denotes the activation heat per molecule of the reaction components. The velocity of a monomolecular reaction Dushman expressed by the equation:

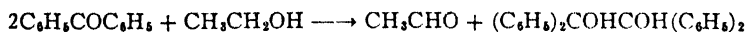
$$\frac{-dc}{dt} = 1.048 \cdot 10^{10} Q_A^{-Q_A/RT}$$

Berthelot and Gaudechon,<sup>12</sup> studying the decomposition of ethyl alcohol, pointed out that ultraviolet light may bring about the same reactions that are obtained with various catalytic agents. The combined action of radiation and the catalyst upon the course of catalytic decomposition of hydrogen peroxide in an aqueous solution was reported by Pissarjewski, Korabelnik and Rynskaja.<sup>67</sup> Graphite, lead dioxide and platinum served as catalysts. The influence of radiation was found to be very specific for the catalysts used. In experiments in which the ultraviolet radiation was applied before catalysis an increase in activity was observed for platinum and lead dioxide. Ultraviolet radiation used during catalysis increased considerably the activity of graphite; but had little effect upon lead dioxide

and still less upon platinum. The 187 per cent increase in the activity of graphite was believed to be caused by the combined action of the illuminated surface of the catalyst and the quanta of energy falling upon it. When smooth and little-active platinum was used together with ultraviolet radiation, the latter caused catalysis to slow down.

Thus there are cases in catalysis in which radiation of various kinds, such as ultraviolet light or x-rays are the primary catalytic agents, while in other cases their action is a secondary one superimposed on the action of the metal catalyst. The more efficient the light energy or the catalyst energy the more ideal are the conditions for a photo- or ordinary catalysis. The difference between photo- and ordinary catalysis is that in the ordinary type the catalyst itself is capable of producing the inductive action, while in photo-catalysis the reactant is activated from an external source—a luminous energy. In ordinary homogeneous catalysis, as stated by Boeseken, “many molecules of the reacting substance are in an active state, while in photo-catalysis active molecules are only those activated by light. A rather continuous contribution of light energy is necessary to produce the conversion of molecules into an active state; otherwise, when the access of light ceases or the molecules escape its reaction, they immediately return into an inert state.”

In differentiating ordinary catalysis from photo-catalysis, the temperature coefficient must be considered also. The temperature coefficient in ordinary catalysis is of the order of that in ordinary chemical reactions because the activity of the catalyst shows the same dependence on temperature as that exhibited by molecules of the reactants. The temperature coefficient of photo-catalytic reactions, on the other hand, is smaller because the activation provoked by vibrations of very high frequencies corresponds to temperatures of thousands of degrees, and the increase of temperature by a few degrees has very little influence. As an example of ordinary catalysis in which a dislocation action is produced without radiation, the catalytic oxidation of alcohol with platinum was considered.<sup>18</sup> The oxidation of primary and secondary alcohols in the presence of benzophenone activated by ultraviolet rays is the example given for a photo-catalytic reaction wherein the aromatic ketone is changed by the ultraviolet light to a “superketone” which plays the same role as atoms of platinum or palladium. As soon as the alcohol is subjected to the influence of the activated ketone, it is oxidized with the formation of aldehydes or ketones, and in the presence of oxygen the benzophenone is continually regenerated. In the absence of oxygen this reaction, which absorbs light energy, occurs as follows:



Boeseken interpreted this photo-catalysis by using Baur's<sup>8</sup> conceptions according to which the energized molecule is electrically polarized, the intramolecular electromotive force depending solely upon the frequency of the absorbed light. In the action of benzophenone upon alcohol, one molecule of alcohol forms a complex with two of activated benzophenone; and under

the influence of this complex two hydrogen atoms of the alcohol molecule are converted into a more mobile state.

In general, however, the radiation hypothesis has not stood the test of experiments. It was shown by Langmuir,<sup>48a</sup> and later by Christiansen and Kramers,<sup>24b</sup> Lewis and Smith,<sup>50b</sup> and Tolman<sup>101a</sup> that the density of radiation of any frequency was insufficient to account for observed reaction rates. It was further shown<sup>25a</sup> that nitrogen pentoxide, for example, has no absorption band corresponding to the frequency which it should have according to the radiation hypothesis. In many cases it was also indicated that illumination with radiation of the calculated frequency produces no increase in the reaction velocity.<sup>25a, 38b, 72a, 102a</sup>

An additional evidence that radiation plays no important role in catalysis, except perhaps in isolated cases, has been offered in Lindemann's suggestion<sup>51a</sup> (later verified experimentally) that the apparent monomolecular character of certain reactions is the result of a time lag between activation by collision and reaction due to a rearrangement of the internal energy, and that consequently at low pressures such reactions would become bimolecular as the rate of the acquisition of energy became slower than that of its rearrangement.

The action of light upon a solid does not always produce a photochemical reaction. Often illuminated bodies do not show chemical changes, but act as a source for the emission of electrons. A so-called photoelectric process may take place under the action of ultraviolet light, resulting in the liberation of electrons. In the case of catalytic reactions, these free photoelectrons may transmit the catalytic activity and if so, the class of catalytic reactions in which light participates should be related to the photoelectric effect. The mechanism of hydrogen peroxide decomposition on platinum exposed to ultraviolet radiation was described by Royter as follows. During the catalytic process electronic streams flow from inactive places of platinum to active centers, the latter playing the part of a carrier for the electrons and transporting them from the hydrogen peroxide molecules present in the inactive field to those molecules which adhere to active centers. In the case of very weak or very strong catalysts the radiation may slow down the process by making difficult the transmission of electrons through hydrogen peroxide molecules to the platinum surface; otherwise the radiation improves the activity of the catalytic agent.

The photoelectric process has been described<sup>26</sup> as an atomic process involving an absorption of radiation from an external source with a resulting emission of electrons. Electrons are emitted from the atom at a definite absorption energy,  $q = h\nu$ , where  $h$  is Planck's constant and  $\nu$  is the frequency of the radiation. The initial velocity with which the electron leaves the metallic surface may be readily determined according to Thomson and Lenard if the maximum potential to which an isolated plate becomes charged on illuminating it with monochromatic light is measured. On the other hand, the work carried out by the electron emitted from a metallic plate or some other source is the product of charge  $e$  and potential  $P$ . The condition for the emission is that the kinetic energy of the emitted electron exceed  $(e.P)$ ; ( $\frac{1}{2}MV^2 > e.P$ ). The velocity of the emitted electron in-

creases with the frequency of the incident light, the energy being linearly related to the frequency:

$$e \cdot P = \frac{MV^2}{2} = h\nu - p$$

where  $p$  is the work done by the electron in escaping. Below a certain minimum frequency which depends upon the surface the photoelectric effect is not observed. If the emission of the electron is accompanied by the liberation of light,

$$\frac{MV^2}{2} + p + h\nu_1 = h\nu$$

where  $\nu_1$  is the frequency of the emitted light. It follows, then, that  $\nu_1 < \nu$ ; in other words, in the photoelectric effect combined with an emission of light, as in the case of phosphorescent substances, the light emitted must have a lower frequency than the light causing the effect. This suggests the possibility that catalysts which emit electrons under the influence of light act similarly to phosphorescent substances. The latter are types of mixed crystals and the difference between their action and that of catalysts may be that the latter instead of emitting light use the separated energy for chemical rearrangements in the system, greatly increasing the velocity of the process. If it is postulated that the catalyst functions not merely by forming intermediate compounds with the reactants, but by itself undergoing changes either in the state of aggregation or the crystallographic structure (crystalline  $\rightleftharpoons$  amorphous), or else that electronic conversions take place which make it harmonize better with the electronic configurations of the reacting components, then a rough similarity between the functioning of the catalyst and that of luminescent substances may be drawn. The appearance and properties of phosphorescent substances may be parallel to those of the catalyst only in the case of catalysts which form mixed crystals. As far as phosphorescent substances are concerned, they usually are mixed crystals and the quantitative proportions of substances making up the mixture are not the only factor in their action. The preliminary treatment in the form of heat induces their activity and supplies the energy emitted as light. Catalysts in their turn depend greatly in their action upon the physical or chemical pre-treatment which brings their activity to a higher energy level and converts them into accelerating agents.

Only in one case, however, were luminescence and catalytic activity related. Schleede, Richter and Schmidt<sup>81</sup> compared the luminosity and the catalytic activity by using two preparations of zinc oxide of different origin in the catalytic decomposition of methanol and found that these properties vary with the method of preparation. Zinc oxide obtained by thermal decomposition of zinc nitrate at 360° (temperature of the catalytic process) showed a fluorescence, although short-lived, when exposed to ultraviolet light, x-rays, and cathode rays, but no catalytic activity. Thermally decomposed (at 360°) zinc carbonate gives zinc oxide which does not show any fluorescence, but does have a strong catalytic activity.

The writers believed that the difference in properties was caused by

differences in the degree of compactness. In the case of the oxide prepared from the nitrate, the luminescence was attributed to the presence of twin planes at the boundaries formed by crystallizing out from the nitrate melt into compact zinc oxide particles; the compactness explains the lack of catalytic activity. The particles of zinc oxide prepared from the carbonate, on the other hand, were not crystallized out from a melt, and had a loose, porous character which favored catalytic activity.

### Resonance Phenomenon in Catalysis

The relationship between time and the values of the kinetic energy  $L$  and the potential energy  $U$  of the electron was expressed by Sommerfeld<sup>87</sup> in the form of the following equation:

$$\int_0^T (L - U) dt = \frac{h}{2\pi}$$

where  $h = 6.55 \cdot 10^{-27}$  erg/second. Sommerfeld showed that the electron would be set free when

$$B = \int_0^T (L - U) dt = \frac{h}{2\pi}$$

and that the kinetic energy of the electron at this time would be

$$L = \frac{h n_0}{2\pi}$$

where  $n_0 = 2\pi\nu_0$  is the characteristic frequency of the electron.

In case a resonance takes place between the electron and the wave length of the illuminating light, the kinetic energy  $L$  is equal to  $h\nu$  (where  $\nu$  is the frequency of the light) and the above principle is fulfilled—the electrons are set free; but in case of an incomplete resonance effect because of the lack of coincidence of the period of vibration of the electron with the period of the impinging wave, the emission may occur if  $\nu > \nu_0$  with a velocity determined from the relationship

$$L = \frac{MV^2}{2} < h\nu_0$$

but at  $\nu > \nu_0$  no free electrons are separated.

The number of emitted electrons is proportional to the intensity of the illumination. It has been ascertained<sup>27</sup> that when the electric field of light is perpendicular to the metallic surface the photoelectric effect is twelve times stronger than when it is parallel to it. On the other hand, the effectiveness of the illuminated surface depends upon its electropositiveness. The more electropositive the metal, the more readily it loses its negative charge under the action of light and the more intense is the effect. Photoelectric currents for caesium, rubidium, potassium and sodium are greater than for zinc, cadmium, aluminum and magnesium. The number of emitted particles is proportional to the intensity of light, but the velocity does not depend on the latter—it is related to the wave length. The

velocity of emitted electrons increases with decreasing wave length of the acting light. There are indications of a maximum at a definite wave length. Pohl and Pringsheim (1910) observed maxima of "selective" photoelectric effect for the following wave lengths: rubidium, 490  $\mu\mu$ ; potassium, 440  $\mu\mu$ ; sodium, 340  $\mu\mu$ , and lithium, 280  $\mu\mu$ . It has not been established whether the selective effect is a general phenomenon or is limited to the alkali metals, because for other metals, if the selective effect exists, it lies at such short wave lengths that the study is made difficult. As for the wave length, Lindemann gave the following simple formula:

$$\lambda = 65.3 \sqrt{A/n}$$

where  $A$  denotes the atomic weight,  $n$  the valency, and  $A/n$  the chemical equivalent of the substance. The maximum value of the selective and normal photoelectric current may be related to the energy of the absorbed wave length and is about  $50.10^{-4}$  coulomb/ calorie for potassium,  $120.10^{-4}$  coulomb/ calorie for sodium, and about  $300.10^{-4}$  coulomb/ calorie for a colloidal surface of these metals, while the normal effect is estimated to be less than  $10^{-4}$  coulomb/ calorie.

London<sup>52</sup> and also Pauling<sup>61</sup> stated that there are two kinds of interchange energy between two atoms: (1) energy due to coulomb forces, and (2) the resonance energy. The resonance effect involves the conception that an electron is not a particle but a charge distributed through space about a region of maximum density, the resonance energy corresponding to the strength of a homopolar bond determined by the distance between atoms. A catalyst is supposed to cause a slight shift in the normal spacing of energy levels so that those of the reactants coincide with those of the product obtained.

With respect to the resonance phenomenon in catalysis, Adadurow<sup>3</sup> states that when the wave length characteristic of the catalyzed substance and that of the catalyst coincide, the latter is suited to serve as a catalytic agent in the reaction. If that should be the case, then it should be possible to calculate beforehand not only the direction of a reaction and its character, but to predict the catalyst to be used, as well as the approximate temperature conditions. Catalysts of a definite wave length would induce definite reactions, each wave length having a definite minimum temperature at which it shows its activity and each wave length possessing a sufficient amount of energy to split the molecule. With the increase in the wave length the catalytic activity decreases. This resonance hypothesis has been illustrated by examples.<sup>3</sup> It has been found experimentally that catalysts with wave lengths 4114-2576Å induce dissociation of  $\text{CaSO}_4 \rightarrow \text{CaO} + \text{SO}_3$ ; those with wave lengths 2576-1546Å cause dissociation to  $\text{SO}_3$ ,  $\text{SO}_2$  and  $\text{O}_2$ , while those with a still smaller wave length, less than 1545Å, give rise to  $\text{SO}_2$  and  $\text{O}_2$ , but no  $\text{SO}_3$ . By using a suitable catalyst, such as manganese dioxide at 600°, the yield of  $\text{SO}_3$  may be increased from 0.18 to 25.85 per cent, while the yield of  $\text{SO}_2$  is kept as low as 54 per cent.

The action of heterogeneous catalysts has been interpreted by Brutzcus<sup>24a</sup> in the light of a resonance existing between inner molecular vibrations of the gas used and those of the catalyst. He supports this interpretation

by the fact that in the case of Pt, H<sub>2</sub>, N<sub>2</sub>, or O<sub>2</sub>, respectively, a great number of spectral lines of the spectrum interval in question coincides within  $\pm 5\text{\AA}$ .

Born and Weisskopf<sup>20a</sup> assume a catalyst may increase reaction rates by holding the reactants in proper juxtaposition for a long time as compared with the duration of a collision. On the other hand, the contact surface may assist in effecting a proper adjustment in energy levels between the initial and final states. The chemical transition in the system occurs by the process of quantum mechanical resonance.

### Adsorption Catalysis

Certain catalytic reactions clearly indicate that they are preceded by an adsorption; such processes are called adsorption catalysis.<sup>62, 84, 96</sup> Adsorption of the reactants is effected through "unsaturated atoms" in the surface of the catalyst. Unsaturation is assumed to vary from atoms completely saturated by neighboring ones to those in which the surface atoms are attached by a single valence to the remainder of the surface, being but one step removed from the condition of atoms in a gaseous state. The greatest catalytic activity is associated with the most unsaturated atoms, and the least catalytic activity with the most saturated atoms in the surface. Since the problem of adsorption in catalytic processes is related to the attraction between the reactants and the catalytic agent, chemical or physical combinations of components must be differentiated. In general, selective chemical adsorption is distinguished from physical and molecular adsorption; chemical adsorption involves valence forces, while physical adsorption involves Van der Waals' forces and is a function of capillarity and the critical constants of gases. The typical Van der Waals' adsorption takes place at low temperatures, while chemical adsorption is characterized by a slow rate of reaction which increases with rising temperature. Since a slow process may imply activated adsorption, compound formation, or a combination of these processes, it is recognized that the rate of adsorption in itself is not a criterion for chemical adsorption catalysis. It has been assumed that processes involving adsorption catalysis, in order to be identified and dealt with quantitatively, must be considered over a wide range of temperature not only for the rate of adsorption, but for the corresponding equilibria as well. Differentiation between "primary" and "secondary" adsorption has been suggested because the first occurs with active adsorbents and depends on primary valence forces, whereas the second is characteristic of inert adsorbents and depends on secondary valence forces. On the other hand, Taylor<sup>96</sup> classified adsorption as "primary" and "secondary" with respect to the reversibility of the process and its energy evaluation. The "secondary" or "reversible" adsorption processes are those normally having small heats of adsorption and small energies of activation, while the "primary" or "irreversible" adsorption processes frequently have high heats of adsorption and moderate or large energies of activation. This latter classification clearly emphasizes the fact that adsorptions with higher activation energies are those of significance in catalytic changes. Thus the type of adsorption to be associated with cata-

lytic processes is assumed to be the "primary," "irreversible," chemical in nature, and activated, characterized further by high heats of adsorption and moderate or large energies of activation.

High catalytic activity in the catalyst surface has been localized in "active centers";<sup>62, 96</sup> in homogeneous, one dimensional linear discontinuities of the surface such as "active spots" identified with crystal edges and their boundary lines;<sup>84</sup> and in every irregularity of crystal growth appearing on the surface as an "active spot" of greater attractive power and therefore greater activity. Admixtures of foreign substances, as well as increased rate of crystal growth favoring the occurrence of these irregularities or imperfections<sup>86</sup> are factors contributing to the activity of catalysts. As for mixed catalysts, there is no change in lattice dimensions as indicated by x-ray diagrams,<sup>33, 53</sup> but rather a disturbance in the regularity of the crystal lattice is made responsible for the increased activity.

### Glow Electric Emission and Catalytic Activity; Electrodynamic Conception of Catalysis

The ability to convert molecules of the reactants surrounding the catalyst into a state of higher activity has been connected with the surface of the catalyst. A parallel has been drawn between glow electric emission and catalytic activity<sup>92</sup> under the assumption that activation follows principally either through collisions between adsorbed gas molecules and electrons emitted from the catalyst surface, or through an emission of ions from surfaces participating in catalytic reactions similar to a thermo-ionic emission in gases. Gas molecules upon approaching the catalyst surface are dissociated into ions and driven away from the surface by kinetic agitation with a probable distribution of velocities. Assuming that activation occurs principally through collision between adsorbed gas molecules and "free" moving electrons, Srikantan,<sup>92</sup> considering the laws of glow electric emission, deduced the following equation:

$$K = Y T^{3/2} e^{-(bT+x)}$$

This expresses the relationship between the velocity constant  $K$  of the reaction and the temperature  $T$ , where  $Y$  and  $b$  are constants and  $x = 2K_1ET/mV$ , in which  $E$  denotes the activation energy, and  $m$  and  $V$  correspond to the mass and velocity of the electron. Srikantan's equation has been proved by the data obtained by Hinshelwood for the catalytic decomposition of ammonia on tungsten and the decomposition of nitrous oxide on platinum. In a narrow interval of temperatures,  $3/2 \log T$  may be considered as constant and then the equation is converted into the Arrhenius equation. Comparing the glow electric emission for various surfaces (Table 7), Srikantan concluded that catalytic activation of gases must be ascribed to the electronic emission from the catalyst surface. There may be stages in the activity of the catalyst and its action may be gradual or impulse-like, resulting in a change in the dynamic state.<sup>56</sup>

The catalyst acts electrodynamically<sup>28</sup> when a force, electrical in nature, believed to be effective at a distance of  $3 \times 10^{-8}$  cm. from the surface and



Table 7.

Surface	Ratio of Mixture	Temperature of Glow °C.
Pt	—	1329
ThO <sub>2</sub> —CeO <sub>2</sub>	98.83 : 1.17	1000
ThO <sub>2</sub> —CeO <sub>2</sub> *	98.97 : 1.03	948
ThO <sub>2</sub> —CeO <sub>2</sub>	99.12 : 0.88	1000

\* Auer mixture emits more strongly than other ThO<sub>2</sub>—CeO<sub>2</sub> mixtures at equal temperature.

assumed to control the thermo-ionic emission of gases, induces a chemical action by the combination of the emitted ions. The emission of ions follows Richardson's equation, their concentration increasing as the inverse cube of the distance from the corresponding surface. Although the electrodynamic conception of catalysis does not relate the catalytic effect solely to the action of ions of the metal catalyst, it does emphasize the fact that ionization proceeds more readily the smaller the radius and the greater the charge of the ion, and that ions of different valences should have their radii limited to definite values.<sup>82</sup> (Monovalent not greater than 0.49 Å; bivalent, 0.7 Å; trivalent, 0.864 Å, and quadrivalent, 0.99 Å).

Bradford,<sup>21</sup> studying the catalytic combustion of carbon monoxide on silver surfaces, investigated catalytic surfaces with respect to their electrical properties. The catalytic and electrical properties of the silver catalyst in contact with both moist and dry mixtures of 2CO + O<sub>2</sub> were recorded for the temperature interval 300–600°. Slow changes of the catalytic activity as a result of sintering of the surface, as well as of the alternative introduction and removal of water were observed. At 500° an increase in the activity of the silver surface manifested itself. This effect was considered to be due not to the decomposition of a pseudo-oxide film on the catalyst surface or an altering of the metal lattice itself at this temperature, but to the origin of a new phase in the surface layers of the metal. This new phase was postulated to be analogous to that resulting from a surface vitrification which, under certain circumstances, takes place on a regular lattice.<sup>30</sup> Bradford's experiments indicate that the change taking place is not, however, enantiotropic in character. The presence of this new surface phase is accompanied by an increased activity and an increase in the surface potential. This is in agreement with the vitrification effect postulated for the surface because polishing or cold treatment of metals leads to an increase in the potential.

### Catalysis from the Standpoint of the Electronic Theory

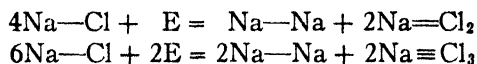
A logical approach to a knowledge of the internal mechanism of catalysis would involve the study of non-catalytic reactions and an examination of the manner in which they change when a catalytic agent influences them. Such an approach is found in the interpretation of catalysis by the electronic theory, according to which an ordinary chemical combination is brought about by the sharing of electrons held in common by two atoms. There is always an interchange of energy between freely moving electrons and atoms. When an electron passes close to an atom then,

provided the energy of the free electron exceeds a certain limit, its total energy may be transferred to the valence electrons lying at the outer periphery of the atom. In strongly polar compounds electrons have been transferred from the outer shells of the electropositive atoms to the outer shells of the electronegative atoms in order to complete stable groups of electrons. The primary valence relationships are dependent upon the number of electrons that can be transferred.

In non-polar compounds, such as many organic substances, a pair of electrons held in common by two adjacent atoms constitutes a single bond, a primary valence. When two or more atoms are combined by pairs of electrons held in common, there are stray fields of forces which are in part due to electrons which form the outer shells of the atoms; these fields result in secondary valences.

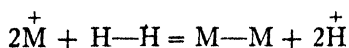
The state when valence electrons are elevated to higher quantum orbits is not stable, and when they revert to their original positions the excess of energy is set free as radiation of characteristic frequencies or in various other ways. The atoms which receive energy from free electrons convert it into monochromatic radiation characteristic of the atom. If the energy of the bombarding electron is large enough, it may tear off the valency electron from the parent atom; this stage corresponds to an "ionization."

Achalme<sup>2</sup> interpreted the mechanism by which a catalyst acts by considering its electronic characteristics. According to this interpretation, a substance acts as a catalyst if it is capable of: (1) supplying electrons to a system, or (2) removing them from it, and (3) producing a simple exchange of electrons. Consequently the electronic hypothesis proposed by Achalme assumes that catalytic reactions are those in which inter-atomic electrons are increased or decreased in number, or in which there is a change in distribution of electronic bonds between atoms and the formation of new molecules. The decomposition of sodium chloride into metal and chlorine by cathode rays, as well as the formation of the allotropic state (conversion of white phosphorus into red, or production of allotropic nitrogen), are examples of reactions made possible by the increase of inter-atomic electrons:

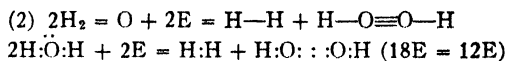
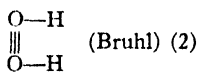
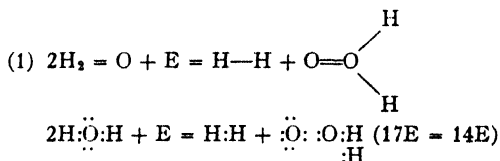
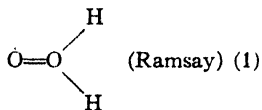


These reactions necessitate also an increase in the valence of the alkali metal (the increase in the number of electrons introduces a change in valencies of atoms present).

Achalme<sup>2</sup> expresses the catalytic influence of Pt, Pd, Ni, etc. upon hydrogenation as follows:



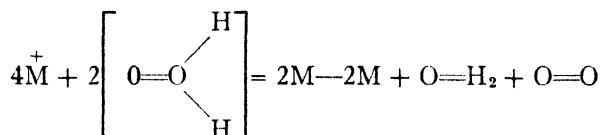
The reaction may be caused by the increase in the number of bonds due to the addition of an electron in the molecule:

Structure of  $\text{H}_2\text{O}_2$ :

However, equations (1) and (2) do not balance electronically, and the structure of hydrogen peroxide is considered definitely:



For the action of metals upon hydrogen peroxide Achalmé postulated the removal of electrons:



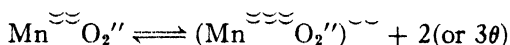
The third class of catalytic reactions occurring with an exchange of electrons Achalmé illustrated by the hydrolysis of sugar by acids or by diastase.

The catalytic effect has been considered also as a function of the maximum kinetic energy of "free" electrons. If the ionization energy of a molecule close to the surface is lower than the kinetic energy of the surface electrons, then ionization takes place and the molecule is adsorbed in a state in which it is able to react. There are metals like sodium, potassium, zinc and aluminum which liberate electrons even under the influence of ordinary visible light provided their surface is fresh and clean. The existence of free electrons in a metal at ordinary temperature was first attributed to the action of infrared radiation,<sup>60</sup> and later free electrons were found in metals at absolute zero, where there is no infrared radiation. This fact led Pissarjewsky and his co-workers<sup>64</sup> to believe that free electrons of a metal serve as a means for coupling with the electrons of the reacting molecules or their atoms, causing their catalytic activity. The number of free electrons depends upon the activity of the metal and is indicated by the order in which metals are placed with regard to the photoelectric effect. Thomson<sup>100</sup> explained the combination of hydrogen with oxygen on heated platinum wire (or a carbon filament) under the action of x-rays not by the action of heat, but by the influence of a stream of electrons set free during the catalytic process. Atoms of platinum, as well as other metals, dissociate into ions and electrons:  $\text{Pt} \rightarrow \text{Pt}^{\infty} + 2\theta$ . According to Pissarjewsky's<sup>64</sup> reasoning, in the case of the hydrogen-oxygen reaction catalyzed with platinum, streams of electrons are set free from the platinum

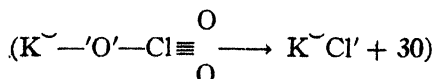
surface with a force sufficient to eject electrons from molecules of the catalyzed substance, producing in the latter a mechanical disturbance of electrons. For example, in the oxygen-hydrogen catalysis, electrons are emitted from hydrogen atoms converting them into positive ions. The electrons thus produced, together with electrons of the stream, are added to the atoms of oxygen to form their negative ions, the latter forming a surface compound with platinum ( $\text{Pt}^{\sim}\text{O}''$ ). This compound is readily converted into the surface compound  $\text{Pt}^{\sim}(\text{O}'\text{H}^{\sim})$ , and finally the negative ions of oxygen 'O' unite with two positive ions of hydrogen ( $\text{H}^{\sim}$ ) to form molecules of water.

The electronic nature of ionic reactions has been proved by Pissarjewsky and Rosenberg<sup>68</sup> in experiments in which a current was produced in metallic plates as a result of a change in the concentration of free electrons.

Pissarjewsky distinguishes two stages in a catalytic process with metals or metal oxides as catalysts. First, the electrons set free from the metal are supposed to be located in the form of a thin layer around the metal. This corresponds to the final state of equilibrium in the first stage; because only fast moving electrons are emitted from the metal under ordinary conditions, those that have a small velocity are pulled back into the metal by the attraction of its ions. In the second stage, the layer of electrons attracts molecules to its adsorption surface; these molecules penetrate inside of the metal forming a solid solution. Any metal oxidizing rapidly and forming an oxide film (like zinc) prevents the formation of a film of electrons and therefore metallic surfaces in order to catalyze properly must be clean. This limitation is true for ordinary conditions, and not for those under which energy in the form of light or x-rays is applied, which may set free electrons with such force that an oxide film does not act preventively and the influence of the state of the surface as well as that of the adsorption factor becomes insignificant. The catalyzing action of metal oxides has been interpreted by Pissarjewsky from the same point of view as that of metals. The scheme for dissociation (although very small, as indicated by the electromotive series) into electrons and ions is presented as follows:



The catalysis of decomposition of potassium chlorate<sup>9</sup> is based on the mechanical action of electrons of the free metal or metal oxide which serves as the catalyst. This action results in the transition of electrons from ions of oxygen to the positive ion of chlorine. The latter gains six electrons and is converted to the negative ion of chlorine which, with the potassium ion, forms a molecule of potassium chloride, while the atoms of the oxygen separate from potassium chlorate and form a molecule of free oxygen:



The reason for this catalysis is assumed to be a mechanical disturbance in the equilibrium of electrons in the potassium chlorate.

If the function of a metal is to induce the transition of electrons between molecules of the catalyzed substance, the latter transferring this action to the neighboring molecules of reacting components, then this postulate implies the existence of catalysis not only on the surface of a catalyst but also in the interface of the catalyst/reactant molecules, and at a distance in the gaseous space among the gas molecules activated by the catalyst. The energy required for catalysis at a distance is transmitted by inelastic\* collisions of the second kind.† Poljakow claimed that the activity of hydrogen activated by palladium is maintained at a distance of about 20 cm. from the catalyst surface.

Recently Kohanenko,<sup>46a</sup> studying the catalytic decomposition of acetone over nickel catalyst, proved definitely the formation of chain carriers on the catalyst surface and the subsequent development of chains in the volume at temperatures as low as 210° and at distances from the catalyst as great as 15–20 cm.

### Properties of Substances Acting as Catalysts

The participation of a catalyst in a chemical reaction is characterized by an optimum temperature under given conditions, such as pressure and time. The catalyst does not change the equilibrium constant of the chemical reaction in which it participates, but it is instrumental in obtaining the final equilibrium state in a shorter time. It is not the mass of the substance involved in the reaction that is essential in attaining equilibrium more rapidly, but a suitable packing arrangement or orientation of the reacting components and of the catalyst in the space in which the reaction proceeds so that the exchange action of the reacting substances, whether it be electrical, magnetic, electro-magnetic, or chemical in nature, is facilitated. A suitable space configuration leads to an advantageous addition of volumes and formation of molecular aggregates. Those elements that have the largest atomic volumes have the largest spaces between the atoms and vice versa. The often observed selective action of catalysts may be explained if their activity is regarded from the point of view of the relative position and distances of active atoms.

From the old space chemistry it is learned that spaces between atoms are relatively large compared with the size of the atoms themselves and that the constituent particles of elements with high atomic volume approach more nearly conditions of gas particles than those of elements with small atomic volumes. Mendeleeff pointed out that the change in chemical activity of alkali metals (from lithium to caesium) is due to an increase in the atomic volume. Elements in a given group having the greatest atomic

\* Elastic collisions are those in which the exchanged energy is entirely the translational energy of the collision. Collisions are inelastic if the atom gains or loses its internal energy.

† Collisions of the first kind are those in which translational energy of the atom or electron is transferred to the internal part of the atom. Collisions of the second kind refer to the case in which the translational energy of the atoms or electrons is transferred from the internal part of the atom.

volume are strongly electropositive; therefore when two atoms of different volume are brought into contact, the attraction of the smaller for the electron in the larger atom is greater than the attraction of the larger for the electron in the smaller atom, and the resultant force usually induces transition from the larger to the smaller atom. Kopp's and Schroeder's rule of the old space chemistry expressed the atomic volume of liquid or solid substances additively (volume additivity principle) as a sum of values characteristic for the space occupied by single components. The simple summation of space constants of the components is not possible when polarization and contraction effects, or a high density of packing, are involved. On the other hand, Kopp pointed out that the atomic volume of a polyvalent element, *e.g.*, oxygen, is not a constant quantity but varies according to the way in which the oxygen atom is united to the other atoms in the molecule. In the form of a carbonyl group,  $> \text{CO}$ , the atomic volume of oxygen was found to be 12.2, while in the form of  $< \text{COC} >$  or  $> \text{COH}$ , the value obtained was 7.8. Similarly, Schiff<sup>80</sup> showed that the carbon atom can also have different values, depending upon whether it is united to another carbon atom by a single, a double, or a triple bond.

In the modern space chemistry, the physical magnitude of the space factor is estimated from the chemical composition and the kind of bonds involved. Modern space chemistry is based on both crystallographic and chemical research.

Biltz<sup>14</sup> and his co-workers contributed greatly by unifying the knowledge of space chemistry obtained from their own investigations, as well as that of Goldschmidt, Pauling and Zachariasen. Instead of the spatial characteristics, such as atomic and ionic volumes, Biltz introduced the corresponding "space increments," *i.e.*, the volume occupied by the particle plus a certain intermediate space adjacent to it. Biltz's space chemistry applies to inorganic compounds, molecular aggregates, organic compounds, and crystallized and amorphous substances such as alloys, silicates, mixed crystals, spinels, etc. Biltz gave the spatial characteristic for almost all substances without mentioning the fact that they may be classified as catalytic agents.

A correlation between the physicochemical properties of a catalyst and the type of reaction for which it is desired has been proposed by Berkman, Morrell and Egloff,\* the spatial characteristics of the catalyst being considered in addition to other related factors such as electronic configuration, magnetic susceptibility, and position in the electrochemical series.

### Spatial Factor in the Choice of a Catalyst

With respect to spatial characteristics, catalysts may be roughly divided into two classes: (1) those with large atomic volume, among which the activity increases with the atomic volume. These are characterized by weak ionic fields and by activation occurring on the surface of the catalyst by means of readily liberated electrons; and (2) those with small

\* Paper presented before the 91st Meeting of the American Chemical Society, Kansas City, Missouri, April 14, 1936.

atomic volumes and a high ionic activity which, within a group of elements, increases with decreasing atomic volume.

Biltz<sup>18</sup> developed definite principles in space chemistry which may be applied also in the estimation of the spatial factor of catalysts. Some compounds, although differing in composition, prove to be equally spaced, exhibiting "isosterism"; others show various space requirements for modifications of the same substance, introducing the conception of "polys-terism." The equality of space, as illustrated in Table 8, assumes that the space requirement of one of the elements of the compounds is practically zero so that the volume of the compound is determined only through the other element and is equal to it. This is the case of many metal oxides in which the space requirement of the positive ion is very small and the atomic space increment is equivalent to that of oxygen contained in them. Thus for this group of catalysts the space requirement is essentially determined by the oxygen and, being equally spaced, they may in many cases substitute for one another in the same catalytic reaction.

Table 8. Equally Spaced Oxides (Biltz).

MO <sub>2</sub>		M <sub>2</sub> O <sub>3</sub>		M <sub>2</sub> O <sub>4</sub>		M <sub>2</sub> O <sub>5</sub>	
Catalyst	Space Increment	Catalyst	Space Increment	Catalyst	Space Increment	Catalyst	Space Increment
WO <sub>2</sub>	19.8	Al <sub>2</sub> O <sub>3</sub>	25.7	Co <sub>2</sub> O <sub>4</sub>	39.8	W <sub>2</sub> O <sub>5</sub>	53.5
MoO <sub>2</sub>	20.0	Cr <sub>2</sub> O <sub>3</sub>	29.0	Fe <sub>2</sub> O <sub>4</sub>	44.5	V <sub>2</sub> O <sub>5</sub>	53.7
SbO <sub>2</sub>	20.0	Ga <sub>2</sub> O <sub>3</sub>	29.1	OsO <sub>4</sub>	46.0	Ta <sub>2</sub> O <sub>5</sub>	55.3
NbO <sub>2</sub>	20.04	V <sub>2</sub> O <sub>3</sub>	29.6	Mn <sub>2</sub> O <sub>4</sub>	47.2	Mo <sub>2</sub> O <sub>5</sub>	56.5
HfO <sub>2</sub>	21.8	MoO <sub>3</sub>	30.1			P <sub>2</sub> O <sub>5</sub>	59.3
SnO <sub>2</sub>	21.6	Fe <sub>2</sub> O <sub>3</sub>	30.3			Nb <sub>2</sub> O <sub>5</sub>	60.0
ZrO <sub>2</sub>	22.0	WO <sub>3</sub>	31.2				
SiO <sub>2</sub>	22.7	Ti <sub>2</sub> O <sub>3</sub>	31.5				
TaO <sub>2</sub>	23.1	Mn <sub>2</sub> O <sub>3</sub>	31.6				
		CrO <sub>3</sub>	33.5				
Average	21.0	Average	32.0	Average	42.0	Average	56.0
Oxygen increment		Oxygen increment		Oxygen increment		Oxygen increment	
2 × 11 =	22.0	3 × 11 =	33.0	4 × 11 =	44.0	5 × 11 =	55.0
Exception:		Exception:				Exception:	
PbO <sub>2</sub>	24.6	Y <sub>2</sub> O <sub>3</sub>	45.2			I <sub>2</sub> O <sub>5</sub>	65.4
UO <sub>2</sub>	24.8	La <sub>2</sub> O <sub>3</sub>	49.6				
ThO <sub>2</sub>	26.4						
Exception:							
MnO <sub>2</sub>	17.0						
TiO <sub>2</sub>	18.9						

The literature on catalysis presents many examples (Table 9) in which for the same reaction a series of equally spaced metal oxides or salt catalysts was chosen empirically.

This same space principle is also applicable to anions containing oxygen and participating as catalysts in ionic salt catalysis. The equality in space requirement is absent for oxides of cations with a specific polarization action so strong that they effect strong contractions (shortening of intermolecular distances) or an increase in the volume as a result of unfavorable geometrical packing. The failure of the volume additivity postulate, in the case of one series of oxides (which may be used as catalysts), was attributed by Biltz to a "packing effect." The space requirement for

individual substances must be considered with regard to the kind of packing and the packing density in the crystal. The packing density ( $K$ ) or "number of space fillings" is calculated from the formula:

$$K = \frac{100 \sum \text{globule volumes}}{MV_0}$$

(Mol volume at 0°K)

in which the globule volumes of single ions are determined for the corresponding coordination number, according to the method of Goldschmidt and Zachariasen.<sup>14</sup>

Bragg<sup>22</sup> stated that dense packing seldom takes place. Substances of the same structural lattice type may vary essentially in the density of packing. For example, zinc oxide and beryllium oxide, both equal in structure and of the Wurtzite crystal type, show a striking difference in the packing effect, namely, zinc oxide has a 44 per cent, while beryllium oxide has a 64 per cent packing density. Equal packing density was found for the oxides of magnesium, nickel, cobalt, iron, manganese, cadmium, calcium, strontium and barium (all of which are of the sodium chloride lattice type), namely, 58 per cent, and for the oxides of cerium, praseodymium, uranium and lithium (all of the fluorite lattice type), 55 per cent. The highest packing density, 64 per cent, was claimed for the oxides of aluminum, chromium, vanadium, beryllium and rhodium, also for ferric oxide and titanium sesqui-oxide.

As indicated in Table 8, due to a close-packed lattice, aluminum oxide, titanium oxide and manganese dioxide all have a space increment value below the average for other oxides of the same group. The oxides of thorium, uranium, yttrium, lanthanum, lead peroxide, and iodine pentoxide are also exceptions to the equally spaced oxides in their respective groups. Alkali and alkaline earth silicates present a similar case due to the high space requirement of the positive element.

Concerning the spatial characteristics of higher and lower oxides used as catalysts as shown in Table 10, the higher oxides are almost equal in space to the lower oxides, provided the comparison is made for the same positive ion. In most cases the space requirement of cations decreases with increasing charge.

The space increments of acid ions serving as catalysts are slightly smaller than those of the free acid as indicated in Table 11. Similarly, the space values for anions of potassium salts of the lower fatty acids are slightly smaller than those of the corresponding fatty acids. A similarity of the space principle is therefore recognized for mineral acids and fatty acids.

If there is a small difference between space increments of the salt and its respective organic acid, it disappears for higher fatty acids or becomes less than the experimental error. For the silver salt, the high polarization action increases the space increment and the difference between the salt and the low molecular weight fatty acid is considerable; but for the higher fatty acids, this difference is negligible.

It was concluded from the old space chemistry<sup>40</sup> that the formates and acetates of heavy metals used as catalysts possess almost equal volumes

(Text continued on page 46)



Table 9. Examples Illustrating Equally Spaced Catalysts

No.	Reaction	Catalysts			
		(with the corresponding spatial factor)			
1	Cyanide synthesis: $\text{CO} + \text{NH}_3 \rightleftharpoons \text{HCN} + \text{H}_2\text{O}$ .	TiO <sub>2</sub> , 18.9	CaO <sub>2</sub> , 21	CeO <sub>2</sub> , 23.9	
2	$\text{HCO} + \text{NH}_3 \rightleftharpoons \text{HCN} + \text{H}_2\text{O}$ .	TiO <sub>2</sub> , 18.9	ZrO <sub>2</sub> , 22	Al <sub>2</sub> O <sub>3</sub> , 25.7	ThO <sub>2</sub> , 26.4
3	Decomposition of ammonia.	CaO <sub>2</sub> , 21.0	SnO <sub>2</sub> , 21.6	SiO <sub>2</sub> , 22.7	
4	Decomposition of CaSO <sub>4</sub> · 2H <sub>2</sub> O $\text{CaSO}_4 \rightleftharpoons \text{CaO} + \text{SO}_3$ .	SiO <sub>2</sub> +	(Al <sub>2</sub> O <sub>3</sub> , 25.7	Cr <sub>2</sub> O <sub>3</sub> , 29.0	Fe <sub>2</sub> O <sub>3</sub> , 30.3
5	Decomposition of HBr.	Al <sub>2</sub> O <sub>3</sub> (195°), 25.7	Cr <sub>2</sub> O <sub>3</sub> , 29.0	Fe <sub>2</sub> O <sub>3</sub> (250°), 30.3	
6	Thermal decomposition of NaCl.  Thermal decomposition of KCl.	Zn (675°), 8.90	Mo (300°), 9.37	W (400°), 9.50	Cd (650°), 12.7
		CO (505°), Fe, 6.50	7.05	Cu (470°), Mn (500°), 7.05	7.26
		V (475°), Zn (510°), 8.2	8.90	Mo (480°), W (490°), 9.37	9.50
7	Oxidation of ammonia: $\text{NH}_3 + 2\text{O}_2 \rightleftharpoons \text{HNO}_3 + \text{H}_2\text{O}$ .	Pt + (WO <sub>2</sub> , 19.8	MoO <sub>2</sub> , 20.0	NbO <sub>2</sub> , 20.4	
		Pt + (Cr <sub>2</sub> O <sub>3</sub> , 29.0	MoO <sub>3</sub> , 30.1	WO <sub>3</sub> , 31.2	Nb <sub>2</sub> O <sub>3</sub> , 37.2
8	Synthesis of methane: $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$ .	Ni, 6.55	Fe, 7.05	Mn, 7.26	
9	Synthesis of methane.	NiO, 11.0	CoO, 11.65	FeO, 11.8	
10	Synthesis of methanol.	ZnO + (UO <sub>2</sub> , 14.3	24.8	Cr <sub>2</sub> O <sub>3</sub> , 29.0	MoO <sub>3</sub> , 30.1
				WO <sub>3</sub> , 31.2	Mn <sub>2</sub> O <sub>3</sub> , 31.6
11	Synthesis of methanol.	ZnO + (MgO, 14.3	11.3	MnO, 13.2	
		ZnO + (Al <sub>2</sub> O <sub>3</sub> , 25.7	29.0	Cr <sub>2</sub> O <sub>3</sub> , 29.0	
12	Synthesis of higher alcohols.	ZnO + (Cr <sub>2</sub> O <sub>3</sub> , 14.3	29.0	Mn <sub>2</sub> O <sub>3</sub> , 31.6	
13	Synthesis of higher alcohols.	Cr <sub>2</sub> O <sub>3</sub> + (NiO, 29.0	11.0	CoO, 11.6	CuO, 12.0
14	Synthesis of formaldehyde.	NiO, 11.0	CoO, 11.6	FeO, 11.8	CuO, 12.0
15	Formation of acetic acid ester.	TiO <sub>2</sub> , 18.9	ThO <sub>2</sub> , 26.4	Al <sub>2</sub> O <sub>3</sub> , 25.7	
16	Decomposition of methane.	Ni, 6.55	Cu, 7.05	Cr, 7.2	
17	Decomposition of methane.	Ni, 6.55	Co, 6.58	Fe, 7.05	
18	Decomposition of methane.	NiO, 11.0	CoO, 11.65	FeO + (NiWO <sub>4</sub> , 11.8	CoWO <sub>4</sub> , 39.4
		Ni vanadate, Co uranate		39.3	39.8
19	Oxidation of acetaldehyde to acetic acid.	Co acetate, 0.005%	Mn acetate, 0.2%	Ni acetate, 0.002%	
20	Oxidation of benzene to phenol.	VO <sub>2</sub> , 18.0	WO <sub>2</sub> , 19.8	NoO <sub>2</sub> , 20.0	NbO <sub>2</sub> , 20.4
				TaO <sub>2</sub> , 23.1	UO <sub>2</sub> , 24.8
21	Oxidation of toluene to benzaldehyde to benzoic acid.	(a) Ni, 6.55	Co, 6.58	Fe, 7.05	Cu, 7.05
		(b) MnO <sub>2</sub> , 17.0	VO <sub>2</sub> , 18	WO <sub>2</sub> , 19.8	MoO <sub>2</sub> , 20.0
				Ag, 10.13	23.1
				UO <sub>2</sub> , 24.8	Cr <sub>2</sub> O <sub>3</sub> , 29.0
22	Water gas shift $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ .	Cu + (ZnO, 14.3	22.0	UO <sub>2</sub> , 24.8	
		Cu + (Cr <sub>2</sub> O <sub>3</sub> , 29.0	29.0	MoO <sub>3</sub> , 30.1	WO <sub>3</sub> , 31.2
					Mn <sub>2</sub> O <sub>3</sub> , 31.6
23	Oxidation of CO for obtaining hydrogen.	NiO, 11.0	CoO, 11.6	FeO, 11.8	
24	Reduction of tar phenols.	Cr, 7.2	Zn, 8.9	Mo, 9.37	W, 9.5
					Al, 9.9
					U, 12.2
25	Hydrogenation of aromatic compounds at temperatures close to their decomposition.	Al <sub>2</sub> O <sub>3</sub> + (NiO, 11.0	CoO, 11.6	MoO <sub>3</sub> , 30.1	
26	Hydrogenation of benzene.	Ni, 6.55	Co, 6.58	Cu, 7.05	Ru, 8.05
					Rh, 8.24
					Fe, 8.46
					Os, 8.36
					Pd, 8.79
					Pt, 9.04

Ni and Pt are found to be most active; the catalytic activity decreases as the elements with the shortest atomic distance in the lattice move away from both extremities.

## Chosen Empirically and Singly for the Same Reaction.

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Table 9

No.	Reaction	Catalysts (with the corresponding spatial factor)				
		NiO, 11.0	CoO, 11.6	FeO 11.8		
27	Hydrogenation of naphthalene.					
28	Hydrogenation of phenols to toluene + methyl cyclohexane.	(a) CoS <sub>2</sub> , 27.1	MoO <sub>3</sub> , 30.1	WS <sub>2</sub> , 32.9	(b) CoS, 15.1	NiS(CoS <sub>2</sub> ) 16.1 63
29	Hydrogenation of wood.	(a) Ni, 6.55 (b) NiO, 11.0	Co, 6.58 CoO, 11.6	Fe, 7.05 FeO, 11.8	Cu; 7.05 CuO 12.0	
30	Hydrogenation of fatty acids or oils.	NiWO <sub>4</sub> , 39.4	Ni <sub>2</sub> SiO <sub>4</sub> , 42.6			
31	Hydrogenation of turpentine to camphor.	Benzene, 69.3	toluene 83.6			
32	Hydrogenation of heavy oils to lighter oils.	Se,	Te,	or their compounds		
33	Hydrogenation of fuels.	NiO, 11.0	CoO, 11.6	FeO; 11.8	WO <sub>2</sub> , 19.8	MoO <sub>2</sub> , 20
34	Destructive hydrogenation of fuels.	WO <sub>3</sub> , 31.2	WS <sub>2</sub> , 32.9	UO <sub>2</sub> ~43		
35	Destructive hydrogenation of fuels.	Cr <sub>2</sub> O <sub>3</sub> , 29.0	MoO <sub>3</sub> , 30.1	WO <sub>3</sub> , 31.2		
36	Dehydrogenation of methane to ethylene-containing gases.	FeS <sub>2</sub> , 23.9	CoS <sub>2</sub> , 27.1	NiS <sub>2</sub> , 28.5	MoS <sub>2</sub> , 31.5	WS <sub>2</sub> , 32.9
37	Dehydrogenation of alcohols.	NiO, 11.0	CoO, 11.6	CuO, 12.0	ZnO, 14.3	
38	Dehydrogenation of isopropanol to acetone.	(a) ZnO, 14.3 (c) Ni, 6.55	TiO <sub>2</sub> , 18.9 Co, 6.58	Ca; 25.6 Fe, 7.05	(b) Li <sub>2</sub> CO <sub>3</sub> , 34.7 Cu 7.05	CaCO <sub>3</sub> , 36.8
39	Dehydrogenation of organic compounds.	(MgO, VO, 11.3 Al <sub>2</sub> O <sub>3</sub> , ThO <sub>2</sub> , 25.4	MnO, 13.2 Cr <sub>2</sub> O <sub>3</sub> ) 29.0	ZnO, 14.3	WO <sub>2</sub> , 19.8	MoO <sub>2</sub> , 20.0
40	Dehydrogenation of alcohol.	Co, Fe + (MnO <sub>2</sub> , 17	VO <sub>2</sub> , 18.0	WO <sub>2</sub> , 19.8	MoO <sub>2</sub> , 20.0	NbO <sub>2</sub> , 20.4
41	Dehydrogenation of solid and liquid paraffinic hydrocarbons to higher olefins.	ZnS, 23.9	CdS, 29.5			
42	Dehydrogenation of ethyl benzene to styrene.	ZnSe, 27.2	ZnSb <sub>2</sub> , 28.7	ZnTe, 33.9	ZnAs <sub>2</sub> , 36.2	
43	Dehydrogenation of isobutylamine to the nitrile of isobutyric acid; turpentine to <i>n</i> -cymol.	MnO, 13.2	ZnO, 14.3	V <sub>2</sub> O <sub>5</sub> , 29.6	WO <sub>2</sub> , 31.2	
44	Condensation of derivatives of paraffinic hydrocarbons to higher alcohols, esters and condensation products.	Al <sub>2</sub> O <sub>3</sub> + (MgO, 11.3	ZnO) 14.3			
45	Condensation of nitrogen-containing products.	Zn <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> , 96.5	Cd <sub>3</sub> As <sub>2</sub> O <sub>7</sub> , 88.9	Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , 96.5		
46	Hydration of ethylene hydrocarbons to 15-20% alcohol.	UO <sub>2</sub> , 24.8	Al <sub>2</sub> O <sub>3</sub> , 25.7	ThO <sub>2</sub> , slightly basic oxides mixed with 26.4		
47	Chlorination of olefins.	MgO, 11.3	Li <sub>2</sub> O, 14.7	CaO, 16.7	Sr 20.7	
48	Halogenation; preparation of phosphorus halide.	ZrO <sub>2</sub> , 22.0	ThO <sub>2</sub> , 26.4			
49	Sulfurization; preparation of benzosulfonic acid.	CuO + (MnO <sub>2</sub> , VO <sub>2</sub> , WO <sub>2</sub> , 17.0 18.0 19.8	MoO <sub>2</sub> , 20.0	TaO <sub>2</sub> , 23.1	Cr <sub>2</sub> O <sub>3</sub> , 29.0	Fe <sub>2</sub> O <sub>3</sub> , 30.3
						Ag <sub>2</sub> O) 31.6
		TiO <sub>2</sub> , 18.9	ZrO <sub>2</sub> , 22.0	Al <sub>2</sub> O <sub>3</sub> , 25.7	ThO <sub>2</sub> , 26.4	
		CuCl <sub>2</sub> , 39.0	ZnCl <sub>2</sub> , 45.8			
		CuSO <sub>4</sub> , 44.5	Na <sub>2</sub> SO <sub>4</sub> , 51.8	V <sub>2</sub> O <sub>5</sub> , 53.7		

which are almost the same as the volumes of equivalent amounts of formic and acetic acid in the solid state. At the same time, the differences in contraction characteristic of free acids and salts were not accounted for. Fischer and Lemke<sup>32</sup> demonstrated the dependence of the anion increments on the charge and the polarization action of the cation for formates. Table 12 shows that the change in space requirement of formate anions is not marked, but proceeds in the same direction as for anions of mineral acids.

(Continued).

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Equal or unequal space requirement for some compounds is considered by Biltz as the result of a definite electronic configuration. He differentiated the following conditions as being related to equal spacing: (1) equal number of total valence electrons; (2) equal number of total electrons resulting in an equal nuclear charge; (3) equal arrangement of inner (non-valence) electrons, and (4) distribution of valence electrons to both elements of the compound. In cases which do not comply with these conditions, unequal space requirements result.<sup>35</sup> Biltz<sup>14</sup> stressed the fact that

Table 10. Space Increments (Compared for Higher and Lower Oxides) (Biltz).

Catalyst Space Increment	Cu <sub>2</sub> O 23.1	Cu <sub>2</sub> ...O <sub>2</sub> 24.0	Ag <sub>2</sub> ...O 31.6	Ag <sub>2</sub> ...O <sub>2</sub> 32.5	Ce <sub>2</sub> ...O <sub>3</sub> 47.9	Ce <sub>2</sub> ...O <sub>4</sub> 47.8	Pr <sub>2</sub> ...O <sub>3</sub> 46.7	Pr <sub>2</sub> ...O <sub>4</sub> 46.6	Ga <sub>2</sub> ...O <sub>3</sub> 30.5	Ga <sub>2</sub> ...O <sub>4</sub> 32.3
Catalyst Space Increment	Tl <sub>2</sub> O 44.0	Tl <sub>2</sub> ...O <sub>3</sub> 45.2	Sn...O 20.8	Sn...O <sub>2</sub> 25.6	Pb...O 23.1	Pb...O <sub>2</sub> 24.6	1/3 Pb <sub>3</sub> ...O <sub>4</sub> 24.7	Sb <sub>2</sub> O <sub>3</sub> 39.2	Sb <sub>2</sub> O <sub>4</sub> 40.0	

Table 11. Space Increments of Anions of Acids and the Corresponding Free Acids Compared (Biltz).

Acids Acid Ions Free Acids	Nitric 28.0 33.0	Metaphosphoric 33.5 37.0	Iodic 36.0 36.5	Sulfuric 39.0 45.0	Orthophosphoric 39.0 47.0	Perchloric 40.5 45.0	Selenic 41.0 46.0
Potassium formate 27	Potassium acetate 42	Potassium palmitate 233	Potassium stearate 260	Silver acetate 39	Silver stearate 253		
Formic acid 29	Acetic acid 45	Palmitic acid 233	Stearic acid 260	Acetic acid 45	Stearic acid 260		

Space Increments of Anions of Salts and the Corresponding Organic Acids Compared.

Table 12. Space Increments of Salts of an Organic Acid (Biltz).

Formates of Space Increments	K. 27	Rb. 27	Na. 28	Li. 31	Cs. (31)	} Average 28.8	
Formates of Space Increments	Ba.. 26	Sr.. 27	Zn.. 27	Cd.. 27	Mg.. 28	Ca.. 28.5	Be.. (29) } Average 27.5
Formates of Space Increments	Pb.. 25	La.. 26	Ni.. 26	Co.. 27	Cu.. 28	Mn.. 29	} Average 26.8

some substances, although fulfilling the first three conditions and being of equal structure type as well, may still be unequally spaced as shown in Table 13.

Table 13. Equal and Unequal Space Requirement for Some Compounds (Biltz).

A. Equal Space		B. Equal Space	
Period II:	2 times (2,8); 8	Period II:	2 times (2,8); 8
	AlP 24.5		NaCl 26.3
	SiSi 24.1		MgS 21.0
Period III/IV:	(2,8,18); (2,8,18,18); 8	Period III/IV:	(2,8,8); (2,8,18,18); 8
	CuI 33.0		KI 51.6
	ZnTe 33.9		CaTe 38.2
	GaSb 33.8		
	SeCd 33.6		

The elements of the compound belonging to the same period, II, have the same electronic configuration, for example, 2 times 2,8 and together have 8 valence electrons. Only in the equally spaced substances are the valence electrons held at least partly by both elements of the compound, while in the unequally spaced substances these valence electrons are held completely by one element. It has been pointed out that this type of space equality is found not for true salts with relatively fixed ions, but rather for compounds with a half metallic binding and with strongly polarized ions.

Among compounds often used as catalysts are the ammoniates, the silicates, and the spinels. The space requirement of complex bound ammonia in ammoniates<sup>14</sup> and ammonium salts has been found to approach in general the value of free ammonia. But individual influences have been recognized, such as the dependence on the change in the anion showing that ammoniates by transference from chlorine to iodine become relatively wide-spaced. The volume additivity principle holds for glass silicates; the oxygen increment for various glass silicates was found to average 11.2, while that of silicon dioxide is 13.6. In sense of space, the glass silicates are considered as being placed between liquids and crystals. The spatial factor for these silicates depends upon their composition, it being necessary to ascertain how much silicon dioxide is present in excess and how much in a combined state. Among the acid potassium glass silicates, potassium tetrasilicate ( $K_2Si_4O_9$ ) has the greatest proportion of silicon, while among acid sodium silicates, sodium disilicate ( $Na_2Si_2O_5$ ) is richest in silicon.<sup>14, 106</sup>

Regarding the change of space for spinels,<sup>14</sup> a regular widening influence is observed in the case of trivalent metals. The  $Fe\cdots$  spinels are more widely spaced than those of  $Cr\cdots$ , and  $Cr\cdots$  more than  $Al\cdots$ , the latter being slightly different from the  $Co\cdots$  spinels. This series is explained

by the influence of the "closed" electronic configuration in the case of  $\text{Fe}\cdots$ . The variation in space requirement of the bivalent metals indicates clearly the contracting effect of manganese in aluminum spinels, while it is considerably weaker for iron spinels. With the exception of cadmium-iron spinel, the molecular volumes for iron spinels are quite constant.

The spatial characteristic of the catalyst itself may be related to specific catalytic reactions, and this is seen from catalytic dehydration. Catalytic dehydration should be successful with compounds which are readily hydrated. It is not the hydration of the whole molecule, but the hydration of the cation which is essential. Remy<sup>71</sup> found that for a series of compounds with the same anion the hydration of the cation increases with an increase in its valence. Jones<sup>46</sup> proved that the hydration varies inversely with the atomic volume and that the hydration for the cation increases in the series:  $\text{H}_2\text{SO}_4 < \text{Rb}_2\text{SO}_4 < \text{Al}_2(\text{SO}_4)_3 < \text{K}_2\text{SO}_4 < (\text{NH}_4)_2\text{SO}_4 < \text{Na}_2\text{SO}_4 < \text{Li}_2\text{SO}_4 < \text{MgSO}_4 < \text{ZnSO}_4 < \text{CuSO}_4 < \text{MnSO}_4 < \text{NiSO}_4$ . Aluminum is the only exception in this series due to the complex hydrates of the molecule.

Parravano<sup>60</sup> stated that there is a correlation between the increase in the parameters of the lattice and the increase in the catalytic activity. In decomposing aluminum chloride ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) at  $180\text{--}450^\circ$ , Parravano obtained aluminum oxide,  $d = 2.2$ , with a very good adsorption ability and a high catalytic activity for the dehydration of ethyl alcohol which, on heating up to  $600^\circ$ , was converted irreversibly into a modification of higher density,  $d = 3.5$ , having no adsorption ability and unable to dehydrate the alcohol. By means of optical and x-ray measurements, Parravano obtained evidence for the fact that the distinction between the two modifications is due to varying distances between atoms of the lattice. The change in the structure of the catalyst which affected the catalytic properties was due to a change in the parameters accompanied by a change in interatomic distances on the surface. From this Parravano concluded that with an increase in intermediate distances the free energy of surface atoms increased and with it the number of active centers; this in turn was reflected in an increase in catalytic activity.

### Electrical Properties of the Catalyst

The relationship of the catalyzed molecule with the catalyst surface has been connected with the geometrical structures of the two. A relationship has also been proposed<sup>90</sup> between phenomena taking place on the surface of a metallic catalyst and those on a polarized electrode. In studying the influence of polarization upon the catalytic activity of metals, such as platinum black and palladium used in the catalytic decomposition of hydrogen peroxide, it was ascertained that the anodic polarization retarded rather than accelerated the catalytic activity of platinum, while the cathodic polarization increased the catalytic activity by more than 50 per cent.

Horiuti and Polanyi<sup>99</sup> discussed the overvoltage found in the platinum-catalyzed, reversible transition of hydrogen from dissolved hydrogen gas

into molecules of water. In the electrolytic formation of hydrogen from water, the reason for the hindrance or overvoltage which is found, lies either in the transition of hydrogen ions from water to the state of atoms adsorbed on the electrode, or in the formation of hydrogen molecules from these adsorbed atoms. It was observed that the ionization velocity of the hydrogen depends upon the composition of the aqueous solution, being faster in pure water than in acid or alkaline solution; thus the hindrance in the electrolytic formation of hydrogen must occur during the transition of hydrogen atoms from the platinum catalyst into the solution.

The evidence of a relationship between oxygen overvoltage and catalysis was considered by Garrison and Lilly.<sup>39</sup> They determined the oxygen overvoltage on polished electrodes of nickel, cobalt, iron, iridium, platinum and gold, as well as the depolarization velocity of the oxygen gas for these electrodes, and found that the overvoltage increases in the above sequence of metals, while the depolarization velocity decreases in the same manner. Applying the statistical method, Garrison and Lilly established a relationship between the velocity of the ionization of oxygen  $V$  and the corresponding overvoltage by the expression:

$$\ln V = A (\text{overvoltage}) + B$$

in which  $A$  and  $B$  are constants.

Suhrmann and Coesch<sup>93</sup> stated that changes in the relative catalytic activity of the metal surface with respect to the recombination of hydrogen atoms may be interpreted through the polarization effect of hydrogen atoms in the electric field of the metal surface. Isgarischew and S. Berkman<sup>43</sup> in their hydration theory of overvoltage proved experimentally that overvoltage and polarization are related to the hydration of ions. With an increase in the hydration of the cation, the hydration of the anion decreases (according to Le Chatelier's principle), and the discharge of the anion occurs at a lower potential. In other words, with an increase in the hydration of the cation, the potential necessary for the electrolytic decomposition decreases in the series shown in Table 14.

Table 14. Overvoltage and the Hydration of Ions (Isgarischew and S. Berkman).

Salt		Rb <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	Li <sub>2</sub> SO <sub>4</sub>
H		14	16	17	66	120
E		1.265	1.215	1.200	1.179	1.175
Salt	MgSO <sub>4</sub>	ZnSO <sub>4</sub>	CuSO <sub>4</sub>	MnSO <sub>4</sub>	NiSO <sub>4</sub>	NiSO <sub>4</sub> + H <sub>2</sub> SO <sub>4</sub>
E	1.165	1.160	1.127	1.075	0.970	1.200
H = Hydration of the cation				Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	
E = Potential				1.235	1.370	

When the cation is heavily laden with water, the electrode process is made more difficult or proceeds more slowly than in the case of more simple hydrates, and the overvoltage or polarization is increased. As mentioned above, an increase in cathodic polarization or a decrease in anodic polarization augments the catalytic activity.<sup>90</sup> Thus there exists a relationship between the hydration ability of the cation and its atomic volume on the one hand; on the other hand, the hydration ability and overvoltage or polarization and the catalytic activity are logically related.



With respect to alloys or intermetallic compounds frequently used as catalysts, it is likely that the further apart two metals stand in the electrochemical series the higher the catalytic activity of the alloy. This rule is analogous to the fact that the further apart two metals are in the electrochemical series, the greater the E.M.F. of the current generated by them as plates of a voltaic cell.

Table 15 presents a list of alloy-catalysts empirically chosen by in-

Table 15. Alloy-Catalysts Chosen in Conformity with the Electrochemical Series.

Reaction	Catalyst-Alloy
1. Reduction of acetone. <sup>46</sup>	Cu-Cr
2. Hydrogenation of benzene. <sup>45a</sup>	Cu-Cr
3. Hydrogenation of fatty oils. <sup>47</sup>	Cu-Cr
1. Reduction of phenol. <sup>3</sup>	Cu-Mg
2. Hydrogenation and dehydrogenation of organic compounds. <sup>3</sup>	Cu-Mg
3. Catalytic reactions. <sup>32</sup>	Cu-Mg
4. Hydrogenation of borneol. <sup>5,4</sup>	Cu-Mg
5. Reduction of acetone. <sup>60</sup>	Cu-Mg
1. Synthesis of methanol. <sup>21</sup>	Cu-Zn
2. Hydrogenation of sludge from coal and oil. <sup>68</sup>	Cu-Zn
3. Hydrogenation of fuels. <sup>34</sup>	Cu-Zn
1. Hydrogenation of borneol. <sup>4</sup>	Cu-Ca
2. Various catalytic reactions. <sup>33</sup>	Cu-Ca
1. Catalytic reactions. <sup>33</sup>	Cu-Mn
2. Catalytic oxidation. <sup>8</sup>	75% Cu + 25% Mn
1. Catalytic oxidation. <sup>8</sup>	90% Fe + 10% Cu
2. Catalytic reactions. <sup>32</sup>	40% Cu + 20% Mg + 40% Ni
3. Catalytic reactions. <sup>32</sup>	50% Cu + 10% Zn + 40% Ca
4. Catalytic oxidation. <sup>8</sup>	60% Cu + 25% Mn + 10% Rb
5. Hydrogenation of borneol. <sup>5</sup>	Cu + Al + Zn
1. Desulfurization of hydrogen used for hydrogenation.	Hg-Pb; Hg-Cd
2. Hydrogenation processes.	Na-Hg (Mn, or Pb)
1. Pressure hydrogenation of coal. <sup>68</sup>	Ag-Cr
2. Hydrogenation and cracking of petroleum hydrocarbons. <sup>7</sup>	Sn-Bi
3. Hydrogenation of borneol. <sup>5</sup>	Pt-Na
1. Water synthesis at elevated temperature. <sup>55</sup>	Fe, Ni, Co alloyed to Rh, Pd, Ir, Pt
Reaction Exceptions	Catalyst-Alloy
1. Oxidation of ammonia: <sup>65</sup> $\text{SO}_2 \rightarrow \text{SO}_3$ $\text{KNO}_2 \rightarrow \text{KNO}_3$ $\text{K}_2\text{SO}_3 \rightarrow \text{K}_2\text{SO}_4$	Rh-Pt or Pt group (at room temperature).
2. Water synthesis. <sup>57</sup>	
1. Hydrogenation of borneol. <sup>5,4</sup>	Ni-Pb
2. Pressure hydrogenation of fuels. <sup>35</sup>	Ni-Zn
3. Preparation of hydrogen. <sup>72</sup>	Ni-Cr
4. Hydrogenation of benzaldehyde. <sup>22</sup>	Ni-Al (1 : 1)
5. Hydrogenation and dehydrogenation of organic compounds. <sup>3</sup>	Ni-Mg
6. Hydrogenation of hydrocarbon oils (600–800°).	Sn-Fe

vestigators; their choice can be interpreted in conformity with the above rule of the electrochemical series.

In analyzing other characteristics contributing to the catalytic activity of metals combined as alloys, the total electronic space  $\Sigma V_E$ , corresponding to the difference between the atomic volume and the ionic volume, and the single electronic space  $V_E$ , which is the total electronic space<sup>72</sup> divided by the number of valence electrons, were also considered. In the case of metals, the outer valence electrons are those which essentially determine the electronic space:

$$\frac{\Sigma V_E}{n} = V_E$$

The values are shown in Table 16.

Since there is a strong variation in space requirement with change in the charge of the ion itself, and since the greatest electronic space corresponds to the smallest ionization voltage for the transition of the atom into the ion, the ionization potential may be related to a "catalytic potential." On the other hand, the greater the single electronic space  $V_E$ , the greater the compressibility.<sup>73</sup> If the compressibility factor essential to the formation of an alloy is small, then the deviation from the space additivity law is small too. It is plausible that the strongest catalytic activity for an alloy is to be expected when an element with a large electronic space is combined with an element with a high ionization voltage, for example, a

Table 16. Catalyst as an Alloy—Electrochemical Series.

Catalyst	Cs	Rb	K	Na	Li	Ba	Sr	Ca	Mg	Al
Atomic volume.	65.9	53.1	43.4	22.8	12.6	37.3	33.2	25.6	13.8	9.9
Ionic volume.	26.0	20.0	16.0	6.5	1.5	16.0	11.0	6.5	2.0	
$\Sigma V_E$	40.0	33.0	27.0	16.0	11.0	21.0	22.0	19.0	12.0	10.0
$V_E$	40.0	33.0	27.0	16.0	11.0	> 10.5	11.0	9.5	6.0	3.3
Ionization.	3.9	4.2	4.3	5.1	5.4	15.1	16.7	17.9	22.6	53.0
Electron volt.										
Compressibility.	65.0	40.0	31.0	15.3	8.8	10.2	8.3	5.6	2.8	1.4
$\beta \cdot 10^4$										

Catalyst	Cr	Mn	Zn	Cd	Tl	Fe	Co	Ni	Sn	Pb	H
Atomic volume.	7.2	7.26	8.9	12.7	16.9	7.05	6.6	6.55	16.0	17.9	11.4
Ionic volume.			3.0	6.0	6.0	4.0	3.6	2.0	2.0	5.0	
$\Sigma V_E$			6.0	7.0	11.9	3.05	3.6	4.55	14.0	13.0	
$V_E$			3.0	3.5	3.7				3.5	3.2	
Ionization.			27.2	25.8					93.0	98.0	
Electron volt.											
Compressibility.			1.7	2.1	2.3		High		1.9	2.2	
$\beta \cdot 10^4$											

Catalyst	Sb	Bi	Cu	Hg	Ag	Pd	Pt	Au	Ir	Rh	Os
Atomic volume.	18.1	21.0	7.0	13.8	10.1	8.8	9.04	10.1	8.46	8.24	8.36
Ionic volume.	—	8.0	5.0	8.0	9.0	4.0	—	—	1.0	1.0	0.0
$\Sigma V_E$	—	13.0	2.0	6.0	1.0	4.8	—	—	—	—	—
$V_E$	—		2.0	3.0	1.0						
Ionization.			7.7	29.1	7.5			9.3			
Electron volt.											
Compressibility.			0.7	—	1.0			0.6			
$\beta \cdot 10^4$											

Potential for the Metals of the Electrochemical Series

	Mg	Mn	Zn	Cd	Tl	Fe	Co	Ni
$E_A$	-1.72	-1.089	-0.796	-0.426	-0.396	-0.46	-0.32	-0.26
		Sn	Pb	H	Sb	Bi	Cu	Ag
$E_A$		-0.19	-0.148	$\pm 0.000$	+0.160	+0.295	+0.307	+0.775

$E_A$ —potential related to the hydrogen electrode

noble metal with an alkali metal. The energy evaluation and space chemistry of alloys indicates a dependence on the change of the electronic state which does not consist in a transition of electrons from one atom to another, as is the case in salt formation, but is an increase in density of the free electronic gas.<sup>17</sup>

### Electronic Configurations in the Catalyst

The electronic characteristics of catalysts are responsible for different processes.<sup>74</sup> In the catalysis of a solid by a solid there are many cases, as shown in Table 17, where the catalyst is identical with the positive ion of the compound catalytically decomposed. The presence of a strong deformation of the electronic orbits<sup>28</sup> of the oxygen ion which characterizes this group of catalysts is postulated as an explanation. The action of the catalyst is related to the deformation under the assumption either that the catalytic field of the surface of the solid catalyst is the same as the deformation field of its positive ions or that the electrons of deformed ions participate in the catalytic process.

Table 17. Catalysis of a Solid by a Solid.

Reaction	Catalyst
$10\text{KMnO}_4 \rightarrow 2\text{K}_2\text{MnO}_3 + 3\text{K}_2\text{MnO}_4 + 5\text{MnO}_2 + 6\text{O}_2$	$2\text{K}_2\text{MnO}_3 + 3\text{K}_2\text{MnO}_4 + 5\text{MnO}_2$
$2\text{AgMnO}_4 \rightarrow 2\text{AgMnO}_3 + \text{O}_2$	$\text{AgMnO}_3$
$2\text{Ag}_2\text{O} \rightarrow 4\text{Ag} + \text{O}_2$	$\text{Ag}, \text{MnO}_2, \text{Pt}$
$\text{CdCO}_3 \rightarrow \text{CdO} + \text{CO}_2$	$\text{CdO}$
$\text{PbCO}_3 \rightarrow \text{PbO} + \text{CO}_2$	$\text{PbO}$
$\text{Ag}_2\text{C}_2\text{O}_4 \rightarrow 2\text{Ag} + 2\text{CO}_2$	$\text{Ag}$

The catalytic decomposition of  $\text{Hg} \equiv \text{O}''$ ,  $\text{Ag}_2\text{---O}''$  and  $\text{K---Mn---O}_4''$  is considered<sup>75</sup> as consisting of an intercrystalline or an intermolecular transfer of electrons from the ion of oxygen to the positive reducing ion, while in the decomposition of  $\text{H}_2\text{---}(\text{O}_2)''$  the decomposition of the molecules into electrons and ions is involved.<sup>66</sup>

The existence and action of free electrons in the metal catalyst can not always be used as an explanation of the catalytic action. The catalytic activity may be related to Swinne's<sup>94</sup> phenomenon of "electronic isomerism." It is postulated that in a unit of a metallic surface there are various groupings of electrons, each grouping having an equal total number of electrons and the same atomic nucleus. Depending on whether or not these electrons belong to atoms capable of dissociating into ions and electrons, there originate active or passive isomers. While an active isomer is dissociated into ions and electrons, the passive isomer does not possess groups of true valence electrons able to attain a free state. Various agents, among them catalysts, may cause the conversion of one electronic isomer into another, accompanied by an intermolecular transition of electrons.

Pissarjewsky linked the catalytic activity with electronic isomerism, and Korabelnyk verified experimentally that in certain cases the possibility of catalytic action through the formation of electronic isomers may exceed the primary factor of the existence of free electrons or high electronic conductivity. Korabelnyk compared the catalytic activity of the catalysts manganese dioxide and lead peroxide in the catalytic decomposition of hydrogen peroxide. If the catalytic activity were due to the action

of the free electrons in these oxides upon the molecules of hydrogen peroxide adsorbed by them, then the best catalyst would be the one that possessed the highest electronic conductivity. According to Fischer,<sup>81</sup> the conductivity of lead peroxide is five hundred and fifty times greater than that of manganese dioxide, while manganese dioxide catalyzes the decomposition of hydrogen peroxide six times as fast as lead peroxide. Thus Pissarjewsky assumed that the catalytic effect is due to the phenomenon of electronic isomerism present in manganese ions and absent in lead ions. Of course, conversion of active electronic isomers into passive isomers may occur in spite of the presence of a catalyst when other influences of a chemical or an electrochemical nature influence the system. The catalytic activity may be improved also through the influence upon the electronic isomerism of a catalyst of other factors such as light. Metals or metal oxides, the atoms and ions of which do not have electronic isomerism, exert their catalytic activity through the action of free electrons combined with the action of charged ions upon the adsorbed molecules of catalyzed substances.<sup>82</sup>

The catalytic activity attributed to surface layers of the catalytic agent may be due to the presence of free electrons, ions and electronic isomers. But there are cases in catalysis, like hydrogenation, in which the principal process is the ionization of hydrogen combined with its ability to penetrate into the inside of the crystal lattice of the metal or metal oxide. It is supposed, for instance, that hydrogen when adsorbed on platinum or analogous metals is converted into its atomic state and simultaneously ionized and that the atomic hydrogen enters more readily into reaction with other molecules.<sup>20</sup>

In order that hydrogen may be drawn not only into the surface layers of the catalyst but also into the inside of the metal lattice where the catalytic process takes place, the existence of a sufficient distance between electronic shells of ions is required. The distance between shells of ions for metals acting as hydrogenation catalysts has been claimed to be limited to 1.25—1.4 Å. According to Pissarjewsky,<sup>86</sup> this establishes a relationship between the ability of a metal to serve as a hydrogenation catalyst and that of molecules or atoms of hydrogen to penetrate into the metal lattice.

Pissarjewsky, using the data of Goldschmidt<sup>84</sup> calculated the electronic distances between shells of ions for manganese dioxide and lead peroxide. The results as shown in Table 18 indicate that there are no material distances between the electronic shells of these ions and that molecules and

Table 18. Electronic Distances between Shells of Ions for Manganese Dioxide and Lead Peroxide (Pissarjewsky).

	$d$	$d'$	$r_m$	$r_o''$	$c$	$d - c$	$d' - c$ (Å)
MnO <sub>2</sub>	1.92	1.83	0.52	1.32	1.84	0.08	-0.01
PbO <sub>2</sub>	2.26	2.15	0.84	1.32	2.16	0.10	-0.01

$d$  and  $d'$  = distances between centers of ions of the metal and of oxygen.

$c$  =  $r_m + r_o''$  (the sum of radii of the metal ion and oxygen ion according to data of Goldschmidt and Pauling).

$d' - c$  = distances between ions.

atoms of hydrogen will not penetrate inside of the lattice of manganese dioxide or lead peroxide and therefore they are not suitable as hydrogenation catalysts in catalyzing the process of  $2\text{H}_2 + \text{O}_2$ .

### Magnetic Properties of the Catalyst

The fact established by Gerlach that a magnetic moment is absent in gaseous atoms of iron, contrary to the ferro- and paramagnetism of metallic iron, indicated to Swinne a relationship between the magnetic properties and electronic isomerism of elements. Electronic isomerism is characteristic of the iron group and in general for the eighth group of the Periodic System. The elements of this group have incompletely built intermediate groups of electrons and show specific properties, especially paramagnetism for their ions (Ladenburg's Rule).<sup>48</sup> These elements are, at the same time, excellent catalysts. This suggests the idea that magnetic susceptibility and catalytic activity are related.

The conception that the presence of "incomplete sub-groups" or "intermediate shell atoms" ("transition elements") not completely taken up by electrons and therefore unsymmetrical, is the characteristic feature of paramagnetism in simple ions, while all ions with closed shells or completely occupied intermediate shells are diamagnetic, was applied by Ladenburg to the Periodic System. He showed that the predominant number of ions containing completely occupied sub-groups have 2 or  $2 + 4 = 6$ ,  $4 + 6 = 10$ , or  $6 + 8 = 14$  electrons and are diamagnetic. Considering the electronic configuration of ions, Ladenburg differentiated the following as paramagnetic:  $\text{Ti}\cdots$ ,  $(\text{V}\cdots)$  ( $\text{V}\cdots$ ),  $\text{Cr}\cdots$ ,  $\text{Cr}\cdots$ ,  $(\text{Mn}\cdots)$ ,  $\text{Fe}\cdots$ ,  $\text{Fe}\cdots$ ,  $\text{Co}\cdots$ ,  $\text{Ni}\cdots$ ,  $\text{Cu}\cdots$ ,  $(\text{U}\cdots)$ , and the group of ions of rare earths:  $\text{Ce}\cdots$ ,  $\text{Pr}\cdots$ ,  $\text{Pr}\cdots$ ,  $\text{Nb}\cdots$ ,  $\text{Sm}\cdots$ ,  $\text{Eu}\cdots$ ,  $\text{Gd}\cdots$ ,  $\text{Tb}\cdots$ ,  $\text{Dy}\cdots$ ,  $\text{Ho}\cdots$ ,  $\text{Er}\cdots$ ,  $\text{Tu}\cdots$ ,  $\text{Yb}\cdots$ .

Experimental results<sup>11, 48</sup> revealed that the saturated oxides of metals which in a neutral or an unsaturated state possess incompletely occupied sub-groups (intermediate shells) have a rather small paramagnetism (Table 19).

Table 19.  
*Paramagnetic*

Oxides (used as catalysts)	$\text{CeO}_2$	$\text{TiO}_2$	$\text{UO}_2$	$\text{MoO}_3$	$\text{WO}_3$	$\text{Cr}_2\text{O}_7$	$\text{MnO}_4$	$\text{CrO}_4$	$\text{V}_2\text{O}_5$
Magnetic susceptibility $\cdot 10^6$	+0.06	+0.066	+0.09	+0.12	+0.20	+0.32	+0.36	+0.61	+0.86

*Diamagnetic*

Oxide (used as catalysts)	$\text{Sc}_2\text{O}_3$	$\text{Nb}_2\text{O}_5$	$\text{Ta}_2\text{O}_5$	$\text{ZrO}_2$
Magnetic susceptibility $\cdot 10^6$	-0.029	-0.04	-0.07	-0.114

Concerning complex compounds also used as catalysts, it is known that only those are paramagnetic which contain atoms with incompletely occupied sub-groups ( $n_k = 3_s, 4_s, 4_s$ , or  $6_s$ , respectively). When the magnetic properties of the complex compounds of chromium, iron, cobalt, nickel and copper are compared<sup>103</sup> with those of their ions, it is found that

the amines of chromium, nickel and copper have almost the same strong magnetism as  $\text{Cr}^{\cdot\cdot\cdot}$ ,  $\text{Ni}^{\cdot\cdot}$  and  $\text{Cu}^{\cdot\cdot}$  ions, while cobaltic amines and iron cyanide are not magnetic. They have rather a magnetism of the type of the saturated compounds of vanadium, chromium, manganese and niobium.

The parallel between magnetic susceptibility and catalytic activity of elements serving as catalysts has been proved experimentally in several instances. Farkas and Sachsse<sup>29</sup> showed that paramagnetic gases such as oxygen, nitrogen dioxide and nitric oxide induce catalytic conversion of  $p\text{H}_2 \rightarrow o\text{H}_2$  in the same manner as ions of the iron group or ions of rare earths. However, no parallel can be drawn between the role of paramagnetic catalysts in this reaction and the part they play in any other known reaction, for the *para-ortho* conversion takes place without breaking or forming chemical bonds; rather, it involves an alteration in the magnetic properties of an existing bond, magnets being naturally good catalysts in producing magnetic disturbances (Kassel). Rosenbaum and Hogness<sup>76</sup> found that iodine atoms catalyze the *para-ortho* hydrogen conversion as a result of their paramagnetism. An attempt has been made to compare the changes in the magnetic properties of certain catalyst mixtures under thermal treatment and their function in the catalytic decomposition of nitric oxide or the oxidation of carbon monoxide.<sup>46</sup> The increase in the activity of the catalyst was found to coincide with the formation of a paramagnetic amorphous skin on the surface which is specific for the nature of the mixed catalysts for definite intervals of temperature.

Baudisch<sup>7</sup> supported also the viewpoint that in the catalytic oxidation of nitrogen-containing substances with pentacyan-iron compounds as catalysts, labile intermediate compounds, such as nitroso iron compounds, exercise a deep influence upon the magnetic state of the central atom and also take part in the oxidation mechanism.

The viewpoint that the course of certain processes and the change in activity can not always be explained through changes in the lattice structure such as crystallographic conversions, but that some other internal transitions in states might influence the changes in catalytic activity was taken by Hedvall and his collaborators.<sup>36, 37, 38</sup> Their investigations concerned the relationship between the ferro-magnetic properties of a nickel catalyst and its catalytic ability with respect to the reactions:  $\text{N}_2\text{O} = \text{N}_2 + \text{O}$  and  $2\text{CO} = \text{CO}_2 + \text{C}$ . The results of these investigations seem to indicate that the disappearance of ferro-magnetism in certain substances may bring about a changed chemical and catalytic behavior without effecting any change in the lattice symmetry.

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## Chapter 2

# Catalysis and Adsorption

### ADSORPTION

Adsorption is an increase in the concentration of a substance on a surface or at the boundary of two phases. The type of adsorption occurring most frequently is positive in character and corresponds to an increase in the concentration at the boundary. When the adsorbed substance does not remain at the boundary but is carried into the adsorbent, the phenomenon is known as absorption or sorption<sup>29</sup> corresponding to a solution in the interior of the adsorbent. The term sorption is often applied to gases adsorbed either on carbon or on metals. Absorption on or solution in metals corresponds to an occlusion.

The division of adsorption into positive adsorption and sorption constitutes the Gibbs-Thomson adsorption principle. The conception of this principle has been extended (W. Ostwald) by considering the possibility of the occurrence of positive adsorption at a boundary as related to the existence of an energy potential diminished on account of changes in concentration. The energy potentials involved in the adsorption phenomenon may differ in nature, namely, they may be of a surface tension, electrical, or chemical type.

Adsorption negative in character is rare. Negative adsorption takes place when the solvent for the substance to be adsorbed is to a great extent adsorbed itself. The concentration of a solution from which adsorption takes place increases after the process of adsorption has been completed, for the apparent adsorption of a substance is then smaller than that corresponding to true adsorption because, due to the adsorption of the solvent, there is an increase in the concentration of the solution. Typical examples of negative adsorption occur in the use of gels or, in general, solvated colloids for which adsorption of the solvent plays a significant part. Adsorption is a reversible process when the final state of equilibrium is independent of the state used in obtaining it; in other words the amount remaining in adsorption after a concentrated solution is diluted is the same as obtained from a solution initially diluted.

But there are cases in which the substance is adsorbed irreversibly with respect to the pure solvent. This type of irreversible adsorption is rather common for colloids undergoing coagulation, or when an adsorbent retains the adsorbed substance as a result of chemical changes occurring during adsorption. Exchange adsorption is a typical case of irreversible adsorption. An exchange adsorption takes place when the adsorbents are insoluble electrolytes, such as silicic acid, kaolin, iron hydroxide, aluminum hydroxide, etc., whereby the anions and cations are adsorbed to an unequal extent.

Exchange adsorption is also well-defined by the use of easily adsorbable salts and acids and organic dyestuffs. In certain cases, only the polar part reacts to exchange adsorption, while the non-polar is adsorbed normally. For example, carbon adsorbs only the basic cation from basic dyes, while the anion is retained wholly by the solution. Silicic acid and kaolin, acidic in character, are dyed by basic dyestuffs.

For the interpretation of exchange adsorption, which is a typical example of polar adsorption, electric concepts were used. The ion of an adsorbent which is acid in nature and negatively charged attracts the positively charged ion and, in order to maintain the electric neutrality of the solution, the opposite charged ion must pass into solution. This effect is a function of the mobility of the latter ion. Electrical concepts are insufficient to explain pure polar adsorption when dealing with two adsorbents one of which has a greater polar adsorption than the other and both carrying different electric charges. Equal series of adsorption of dyestuffs obtained in this case prove that the electrical concept alone is insufficient.

The forces at the surface of a solid, the adsorption and catalytic phenomena due to these forces are highly dependent on the type of the solid. Harkins<sup>19a</sup> classifies solids in five general types:

- (1) Ionic crystals (salts)
- (2) Metals (valence electrons "free")
- (3) Semi-conductors
- (4) Valence crystals (diamond, graphite, carborundum)
- (5) Molecular crystals ( $N_2$ ,  $O_2$ , organic compounds).

The attractive forces in ionic solids such as sodium chloride, are principally of the coulomb type; that is, the force of attraction varies inversely as the square of the distance between ions of unlike sign. However, the attraction is not purely coulombic, since polarization and van der Waals' forces are involved too, and these in some instances are made evident by such phenomena as the change of lattice. Metals are characterized by a very high conductivity for electricity and heat, and by their very high reflectivity and adsorption of light. They may be considered as a lattice of positive ions, the charge of which is neutralized by a number of relatively negative electrons equal to the sum of the charges of these ions. These free electrons belong to the whole lattice, and not to any individual atom. According to Pauli's principle only two electrons (excluding spin) can occupy one quantum level, and therefore the number of energy levels is enormous because it is equal to half the number of "free" or conduction electrons. The atoms of the non-metallic compounds are united into molecules by the covalent bond or electron pair. This type of bond unites carbon, hydrogen, nitrogen, and other atoms into the enormous number of organic molecules and it is found also in many of the Werner's coordination compounds, especially of the metallic element of the second and third transition groups. The electron pair bond may be weak as in  $I_2$ , but may be much stronger, as in  $\equiv C-C\equiv$  or  $\equiv C-H$ , than ionic or metal bonds. The strength of the carbon-carbon bond in the diamond is responsible for the very great hardness and extremely high cohesion of this material. Other sub-

stances similar in these respects are Si, SiC, and B<sub>4</sub>C. The low cohesion and the accompanying softness and low melting and boiling points of organic substances are due to the mobility of hydrogen to form more than one electron pair bond. The result of this is that self-sufficient molecules are formed, and these, in hydrocarbon solids, are bound together by relatively weak van der Waals' forces. The breaking apart of a crystal of this type occurs between molecules and not between atoms.

(1) Coulombic expulsive forces characteristic of ionic solids may be expressed through the potential  $V = \frac{e_1 e_2}{R}$ , a scalar where  $e$  represents the charge on the ion and  $R$  the distance between ions of unlike charge. Then  $F = \Delta V = \frac{e_1 e_2}{R^2}$ , a vector.

(2) Solids may contain ions and dipoles. In this case, of ion-dipole forces, the energy of attraction decreases more slowly with increasing distance and

$$V = \frac{e\mu \cos \theta}{R^2}$$

where  $\mu$  is the dipole moment of the dipole and  $\theta$  is the angle between the direction of the dipole and the straight line which connects the ion and the center of the dipole. The mutual energy of the two dipoles is in general

$$V = \frac{M_1 M_2}{R^3} (\cos \gamma - 3 \cos \theta_1 \cos \theta_2)$$

in which  $\gamma$ ,  $\theta_1$ , and  $\theta_2$ , are the angles involved. If an atom and an ion interact, the energy decreases even more rapidly with the distance.

$$V = \frac{a_z^2 e^2}{2R^4}$$

in which  $e$  is the charge on the ion and  $z$  the charge on the nucleus of the atom. Such a force acts also between an ion and a dipole, in which case it becomes a function of the dipole moment and the angle  $\theta$ .

Van der Waals' forces are the relatively weak forces which act between complete molecules or single atoms which have no free valence bonds, and which are not ionic, and do not contain permanent dipoles. They act to bind together such atoms as those of the rare gases, He, Ne, Ar, Xe, Kr, and molecules of the difficultly liquefiable gases, such as N<sub>2</sub>, O<sub>2</sub>, CO, CH<sub>4</sub>, and between all non-polar organic molecules in liquids and solids. Harkins offered the following explanation of van der Waals' forces helpful in understanding their nature: at relatively large distances and over a long time a molecule interacts with another as if both were symmetrical, but instantaneously and at smaller distances it acts as a dipole on account of an instantaneous lack of symmetry in the electronic system. Such an atomic dipole induces a polarization in an adjacent atom. Thus van der Waals' forces may be considered to be to a considerable extent of the high-frequency type. The extent of the polarization depends upon the strength of the dipole moment of the first atom, the polarizability of the second, the inverse

cube of the distance, and the angle between the dipole axis and the line between the atoms. The induced dipole acts upon the original one and the total effect is an attractive force which varies as the polarizability of the second atom, the square of the dipole moment of the first and the seventh power of the distance. The relations may be expressed by

$$V \propto \frac{1}{R^6} \quad \text{or} \quad F \propto \frac{1}{R^7}$$

It is generally recognized that the mechanism of adsorption is based on the principle that the molecules in the surface of an adsorbent have an attraction for the substance to be adsorbed. The attraction is mutual and is believed to be brought about by the same type of binding force, although different systems exhibit a wide variation in the strength of the adsorption binding. Many theories have been proposed with regard to the character of the forces acting between atoms or molecules.

Thomson's theory<sup>62</sup> considers the forces acting between atoms as arising from corpuscles and positive electricity. He further considers these forces as depending not only on the kind of atoms present in the molecule, but on the orientation of these atoms as well, being determined chiefly by the distance between the atoms. Sutherland thought that invariable electric doublets contained within the atom resulted in forces between atoms, the molecules being held together by the attraction between the doublets. Therefore the force exerted by an atom may be characterized by an electric doublet contained in each atom and the corresponding electrostatic moment. For non-metals the electrostatic moment is proportional to the volume of the atom, while for metals it is assumed to be proportional to the linear dimensions of the atom. Thomson, on the other hand, differentiated between chemical compounds having electrically neutral atoms from those with atoms charged either positively or negatively. He assumed that when atoms of a molecule are charged, much larger forces are exerted between molecules than is the case when their atoms are not charged. This is due to the electrostatic moments formed between molecules. The poles of the doublet are more widely separated in the class of compounds in which the atoms are charged, while in the class of compounds in which the atoms are electrically neutral the two poles of any doublet are in the same atom.

Abegg's theory regards each atom as exerting either an electropositive or an electronegative valence the sum of which should equal eight. The electropositive valence should equal the number of mobile corpuscles in the atom, while the electronegative valence should correspond to the difference between eight and the number of mobile corpuscles. This valence theory considers compounds which do not contain charged atoms more elastic because these atoms have twice as many bonds as in molecules containing charged atoms. Thomson's theory regards an atom as having all corpuscles fixed and incapable of exerting a great attraction on other atoms. The state in which all corpuscles in the atom are held by forces acting upon them is called the state of saturation.

Polanyi<sup>40</sup> advanced the viewpoint that adsorption forces of free atoms are saturated by the binding of molecules and that they originate through

a mutual orientation. He postulated as proof for this the phenomenon of absolute saturation expressed in the fact that adsorption forces acting upon a molecule  $F_{AB}$  are always smaller than the sum of adsorption forces acting upon free atoms  $F_A$  and  $F_B$  ( $F_{AB}$  adsorption force acting upon the molecule, and  $F_A$  and  $F_B$  forces of the free atoms). The orientation is considered fulfilled by the mutual approach of molecules followed by a mutual deformation of each other in such a manner that the respective components are oriented favorably for attraction by bringing the opposite electric or magnetic poles of the molecules as close together as possible. This idea found further expression in the interpretation of cases in which molecules of a substance are adsorbed on a surface by attachment to a particular atom of the molecule, a type of oriented adsorption, but not related to the deformation of the molecule.

Coolidge<sup>9</sup> is of the opinion that adsorption is due principally not to the surface forces of the liquid itself, but to a class of forces influenced by the specific nature of the components of the system rather than by changes in temperature. This opinion resulted in the formulation of the adhesion hypothesis implying that the adsorbent influences directly every molecule to be adsorbed.

The idea that the force exerted upon each adsorbed molecule is specific with respect to the chemical nature of the molecule but otherwise depends only on its position relative to the adsorbent rather than on temperature or the proximity of other adsorbed molecules, thus differing from a force of molecular dimension, is the principal thought of Polanyi's potential theory of adsorption.<sup>41</sup> In the latter, the adsorption space is a seat of a field of forces the potential of which at every point is the work of the adsorbent carried out on a molecule moving towards this point from infinity. This potential is expressed in the equation:  $\varphi = -RT \ln P$ , where  $P$  is the relative pressure observed when the system has been brought to a degree of saturation.

Milner, Syskowsky and Traube modified this equation:  $\Gamma = CK e^{\frac{\lambda}{RT}}$  relating  $\Gamma$  and  $C$ , where  $\lambda$  is the decrease in potential energy which occurs when one mol of solute passes from the interior of the solution into the surface layer.

Berthelot<sup>7</sup> and Galitzin<sup>15</sup> assumed that the attraction potential of two unlike molecules is proportional to the expression:  $\sqrt{a} \cdot \sqrt{a_2}$ , where  $a$  and  $a_2$  are van der Waals' constants for the corresponding molecules. This equation indicates the non-specific character of forces of cohesion.

Berenyi<sup>5</sup> and Polanyi<sup>39</sup> related adsorption and cohesion in the expression for the adsorption potential:  $Em = K\sqrt{a}$ , where  $a$  is van der Waals' constant and  $K$  the empirical constant of the adsorbent, indicating that the forces of cohesion and adhesion are non-specific in character; the forces of cohesion serve as a self-active mutual deformation.

Langmuir's theory of adsorption<sup>25</sup> neglects the forces of cohesion operating in the presence of adsorbing forces, but emphasizes the significance of unsaturated residual valences in the phenomenon of adsorption and forces of the surface atoms which would otherwise participate in building

up molecules or the crystal lattice. In the case of a crystalline adsorbent there is an equal distribution of points of residual valences on the surfaces, depending on space lattice. At these points lie comparatively few saturated atoms or atomic groups of the adsorbent. The adsorbate is held by secondary (side) valences of ions so that the adsorbent forms rather a true chemical compound with the adsorbate.

Alexeewski,<sup>1</sup> explaining the mechanism of adsorption with reference to distribution of valence forces in the molecular complexes of the adsorbent, differentiated four types of valence forces: (a) the homopolar type characteristic of elementary substances; (b) the heteropolar type of stable compounds like sulfuric acid and sodium chloride; (c) those producing molecular association or the formation of crystalline hydrates; (d) those characteristic of unstable compounds and of adsorption compounds. The variability of the characteristics of valence forces of the fourth type made it possible for Alexeewski to formulate constitutional formulas for various adsorbents, particularly for active charcoal, silica gel, and clays.

Much attention has been given to the problem concerning the nature of adsorption forces in those theories in which it is assumed that they have an electrical origin due to the fact that intermolecular forces are generally of this type.<sup>10</sup> The electrical theories of adsorption forces have been developed chiefly for the adsorption of gases by solid bodies. In general, the molecules of a gas are assumed to be dipoles oriented in the electrical field of the adsorbent.

Lorentz and Lande,<sup>27</sup> Eucken,<sup>11</sup> Jaquet,<sup>23</sup> Hückel,<sup>21</sup> Iliin,<sup>22</sup> Tarassow,<sup>51</sup> Semenschenko<sup>49</sup> and Mokrushin and Essin<sup>34</sup> all contributed to the development of the electrical theory of adsorption of gases. One of the equations for the absorption potential, namely, that given by Hückel, is:  $N_{ads} =$

$C \cdot Q\zeta \cdot e^{\frac{\epsilon}{kT}}$ , where  $N_{ads}$  expresses the number of adsorbed molecules;  $C$ , the concentration in the gas space;  $Q$ , the adsorbing surface;  $\zeta$ , the range of the adsorption power, and  $\epsilon$ , the adsorption potential. It is presumed that  $Q$  and  $\zeta$  are constant within the course of the adsorption process, and that throughout the entire adsorbing surface the potential  $\epsilon$  does not change, *i.e.*, the adsorbing surface is homogeneous. Eucken is of the opinion that the physical character of the adsorbing forces effects adsorption, and his dipole theory assumes that neutral molecules become dipoles through induction on approaching a heteropolar surface and are held adsorbed by electrostatic forces of attraction. Mokrushin and Essin considered adsorbed molecules as "dipoles" or "free ions" and the adsorbent as a surface carrying an electric charge, either positive or negative; the process of adsorption being a neutralization of electric charges. Eliminating chemical action between adsorbed molecules and the adsorbent, electric forces are assumed to be active at a distance of  $10^{-8}$  cm. corresponding to the thickness of the double layer.

Mukherjee<sup>35</sup> calculated the distance between the "primary" ions causing the charge of the adsorbent and found that the distance between chemically adsorbed ions on the adsorbent was considerable when compared with that for molecules ( $10^{-8}$  cm.). Considering the results of Helmholtz and Lamb,<sup>20</sup>

as well as McTaggart's calculation of the density of the charge on the surface of the gas bubbles,<sup>31</sup> Mukherjee obtained an average distance equal to  $3 \times 10^{-6}$  cm. This led him to assume that the surface of the adsorbent consists of a certain number of "elementary places" where adsorption is possible. The number of elementary places is equal to or proportional to the number of "primary" ions causing the charge of the adsorbent. At a maximum adsorption, the charges of the adsorbent are neutralized by the adsorbed free ions of an opposite sign.

Shilow and Lepin<sup>45</sup> conceived the idea that the participation of the adsorbent in adsorption processes was due not only to its electro-capillary forces, but also to its molecular forces as well. They postulated that the adsorbent produces a definite field of forces which is a function of chemical properties of substances participating in the adsorption process and therefore of a specific nature. The adsorption phenomenon was considered by these investigators as the resultant of complex molecular forces of the adsorbent, the substance to be adsorbed, and the solvent. The function of the solvent in adsorption processes is not only that of a self-adsorber but, due to molecular forces, a competitor of the adsorbent in distributing the adsorbed substance between the solid and the liquid phase as well.

Shilow and his co-workers opposed to a certain extent Freundlich's adsorption theory as one of an "exclusive" surface phenomenon due to a change in surface tension with time. This is based on the fact that in many cases, differentiated by the course of adsorption isotherms, either the capillary or the molecular forces assume the leading role. Adsorption in its pure form, according to Shilow, is the expression of forces and properties principally of undissociated molecules; but should diffusion or a continuous transition from a solid to a liquid phase take place, in which case adsorption becomes a simple distribution of the dissolved substance, the above stated viewpoint is inapplicable. The kind of adsorbent, whether porous, loose, or crystalline, is also decisive as to whether molecular or capillary surface forces play a part. Gurwitch<sup>17</sup> explained the adsorption phenomenon as due to physicochemical forces of attraction equivalent to the physical forces of the Newtonian attraction between molecules and the chemical forces of attraction between atoms and molecules in molecular compounds.

The theories suggested with reference to forces acting in adsorption may be divided into two classes; one group of investigators (Langmuir, Harkins) contend that the attractive forces extend primarily to a monomolecular layer, while the second group (Eucken, Polanyi) is of the opinion that they extend to a polymolecular layer. If in homogeneous gas reactions a reaction occurs between molecules or atoms, then in heterogeneous gas reactions a similar reaction takes place, but between molecules or atoms previously adsorbed. In this case the adsorbed gas layer is the actual seat of the reaction and the amount of gas active in the reaction is the amount of gas adsorbed and disposed by the reaction. As postulated in Langmuir's adsorption theory,<sup>26</sup> gas particles meeting a surface on collision are retained at the surface by saturation of the free lattice valences. The number of gas particles retained or adsorbed approach asymptotically a certain limited value given by the monomolecular layer of the surface. The theory and

experiments agree at low, but not at high pressures. If, as assumed by Langmuir, in crystalline adsorbents "elementary spaces" corresponding to a crystal lattice are present on the surface which have unsaturated valences retaining only one atom or molecule, then the experimental disagreement with theory for higher pressures may be interpreted by an increase in the number of "elementary spaces" entering into action. On the other hand, in order that the thickness of an adsorbed film be proportional to pressure over a wide range of pressures, it would be necessary to have a layer many molecules thick. Langmuir expressed mathematically the amount absorbed at a pressure  $p$  by the following equation: 
$$Q = \frac{1}{\frac{a}{p} + b - cp}$$

This equation was derived by assuming that adsorption is due to the fact that a certain time must elapse between the condensation and the evaporation of a molecule and that in the case of strongly adsorbed substances, or when vapor is almost saturated, the condensation and evaporation in the second and subsequent layers must be accounted for. Therefore, the above equation corresponds to a case in which the rate of evaporation in the first layer differs from that of other layers.

The adsorption theory of Eucken and Polanyi assumes a slower decrease in the forces of attraction and, correspondingly, a layer consisting of many molecules. This theory considers the adsorption layer as a kind of atmosphere, the density of which decreases with an increase in the distance from the boundary similar to the atmosphere surrounding the earth. While Langmuir's theory deals with adsorbed molecules "locally steady," Volmer<sup>53</sup> presents proof for the fact that the monomolecular adsorption layer must be considered as two dimensional gases with free-moving molecules in the surface.

Bodenstein, who proposed a method for controlling the thickness of a film when using a metallic adsorbent, such as platinum or palladium in combining hydrogen with oxygen, found that the thickness of the water film can be regulated by the temperature of the adsorbent which may make it very thick or very thin, measured in microns. But, regardless of how high the temperature of the metal may be raised, the minimum thickness of the water film must correspond to one molecule in thickness; if less, the continuity of the film is disrupted.

In adsorption processes the molecules often arrange themselves with the axis of their length parallel to the boundary, or they are directed with one atomic group towards one or the other phase. Hardy, Langmuir<sup>25</sup> and Harkins and his co-workers<sup>19</sup> conceived the notion of the orientation of molecules in adsorption processes. They showed that the molecules of surface active substances, for example, aqueous solution/benzene or aqueous solution/air consists at the boundary of two parts: (a) the polar or active group, which has many unsaturated secondary valences, and (b) the non-polar or inactive group. To the first group belong hydroxyl (OH), carboxyl (COOH), and other oxygen-containing radicals, as well as the  $\text{NH}_2$  group. All of these groups have an additional affinity expressed



in their tendency for association, hydration, etc. The second group is represented by a hydrocarbon chain and is characterized by a very weak molecular field of forces. The unsymmetrically constructed molecules, Fig. 1, are oriented in the boundary between two phases in a very definite manner. The polar group *a* with a great affinity for molecules of the polar phase (hydrophilic group) will be attracted to phase I and appear to be dissolved in it, while the hydrocarbon chain corresponding to the non-polar phase of molecule *b* is pushed out from the polar phase (phase I) and turned towards phase II.

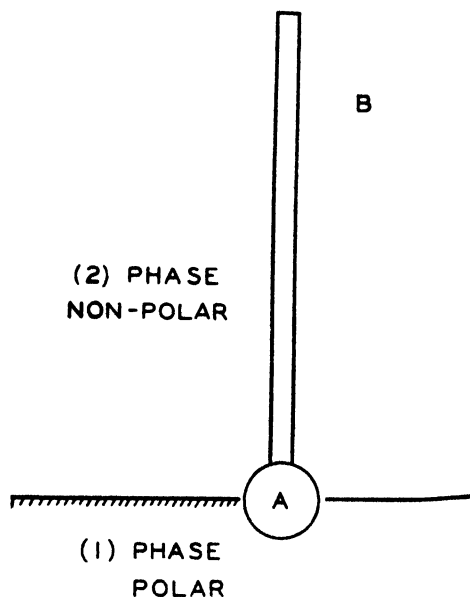


FIGURE 1.

The adsorbed molecules so oriented do not always achieve the maximum orientation even though all places in the layer are taken up by adsorbed molecules, particularly when the layer is saturated; often the action of heat, or rather the movement resulting from it, contributes to a disturbance in the orientation. The structure of the layer is the principal factor in determining the amount of surface energy. As the active polar groups are turned towards the interior of the liquid and the slightly polar groups are projected upwards to form the surface layer, the potential energy for which surface tension is a measure is due to the slightly polar groups; accordingly, molecules in the surface are so arranged that the stray electromagnetic field surrounding the atoms is minimized. Therefore, molecules of a liquid surface are oriented in a definite manner due to the existence of surface tension resulting from an attraction or residual affinity inherent in the molecule.

The equation involving surface adsorption of a substance and its consequent effect on the decrease in surface tension at the boundary  $\delta$ , as well

as on the concentration of the substance inside of the two limiting phases, was formulated by Gibbs<sup>16</sup>:  $\frac{\partial \sigma}{\partial c} = \frac{1}{c} \frac{\partial p}{\partial c} \cdot \Gamma$  where  $c$  denotes the concentration of the substance in solution;  $\sigma$ , the surface tension;  $p$ , the osmotic pressure, and  $\Gamma$ , the adsorption of the substance.  $p$  always increases with an increase in the concentration, therefore:  $\frac{\partial p}{\partial c} > 0$ , and consequently when

$\frac{\partial \sigma}{\partial c} > 0$  and the adsorption is positive ( $\Gamma > 0$ ). Substances, such as water-soluble organic compounds, positively adsorbed at the boundary and decreasing the surface tension, are called "surface active" substances. When  $\frac{\partial \sigma}{\partial c} < 0$ , there is an increase in surface tension and adsorption is negative ( $\Gamma < 0$ ). Substances, such as mineral bases and salts, involved in the adsorption process are surface inactive. When  $\frac{\partial \sigma}{\partial c} = 0$  and  $\Gamma = 0$ , the substances do not influence  $\delta$  to any appreciable extent and no adsorption is observed at the boundary. In case the concentration  $c$  is very low, as in weak solutions or in compressed vapors, the osmotic pressure may be considered as satisfying the Clapeyron-van't Hoff equation for the ideal gaseous state:  $pV = RT$ , where  $V$  equals the volume of one gram mole, or  $V = \frac{1}{c}$ .

Therefore,  $p = RTc$ , or  $\frac{\partial p}{\partial c} = RT$ . Gibbs' equation then assumes the form of:  $-\frac{\partial \sigma}{\partial c} = RT \frac{\Gamma}{c}$ , or  $\Gamma = \frac{-c}{RT} \frac{\partial \sigma}{\partial c}$ , which may be interpreted as indicating that if a dissolved substance lowers the surface tension at an interface, it will be positively adsorbed at that interface.

Reh binder<sup>17</sup> modified Gibbs' equation indicating  $\delta$  as the thickness of the layer in centimeters and  $C_s$  and  $C$  the corresponding concentration of the surface active substance in the adsorption layer from which adsorption proceeds, usually expressed in moles per liter ( $\text{cm}^3$  must be divided by  $10^3$  when converting into liters):

$$-\frac{\partial \sigma}{\partial c} = \frac{\delta RT}{10^3} \cdot \frac{C_s - C}{c}$$

in which  $\frac{\partial \sigma}{\partial c}$  is considered a measure of the ability of a substance to decrease the free surface energy at the boundary where the surface separates. Reh binder suggested measuring the "surface activity" using Gibbs' unit.

$$G = RT \cdot \frac{\Gamma}{c}$$

$$1 \text{ Gibbs} = 1 \frac{\text{erg}}{\text{cm}^2}$$

The adsorption ability is measured with regard to the specific surface of the adsorbent (the size of the surface divided by the volume). The

specific surface is not readily determined; not only the external surface of the adsorbent, but also the internal surface must be accounted for. An adsorbent may be regarded as a definite volume rather than a fixed surface where adsorption processes are concerned. Different values are obtained for adsorption, depending upon whether the accumulation of a substance at a boundary surface is calculated from surface tension measurements at the boundary, for example, water/benzene of varying concentrations, or the amount of a substance adsorbed from water by the total volume of benzene is calculated by the distribution between the two phases (benzene

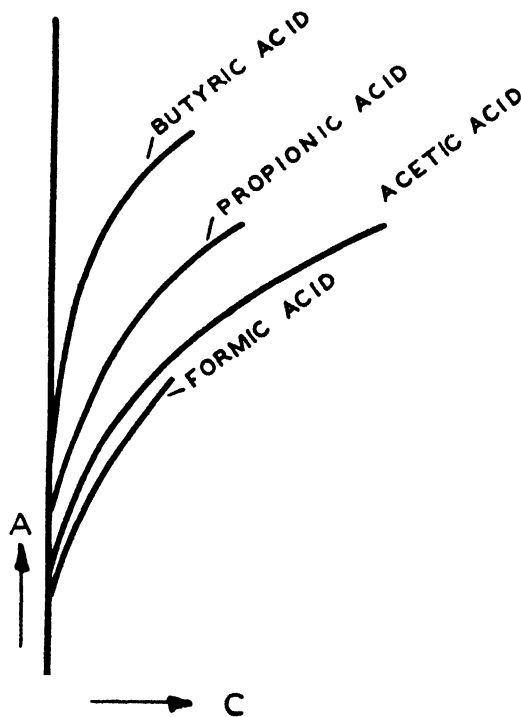


FIGURE 2.

and the aqueous solution). Therefore, the nature and relative value of the "volume" and the "surface" adsorption differs.

The equilibrium attained, after adsorption has taken place, may be established either within a definite or an indefinite time, expressed in seconds or minutes, or when the adsorbent is readily accessible, that is, when it is highly dispersed and readily wetted. When adsorption proceeds rather slowly, it may indicate a rather dense structure of the adsorbent (cocoanut carbon), or it may be due to an inaccessible internal active surface. Sometimes slowness in attaining an adsorption equilibrium may indicate a chemical reaction proceeding parallel with the adsorption process. The concentration of the adsorbed part is not proportional to the concentration of the unadsorbed part present in and in equilibrium with it as is the case of

true solutions. However, it would be the case if adsorption processes followed the Berthelot-Nernst distribution law or the Dalton-Henry law,  $x/m = Kp$ . Therefore, absolute adsorbed concentration,  $C_{abs}$ , is not equal to  $K \cdot C$ , but  $C_{abs} = K \cdot C^n$ , where  $n$  varies between 0.1 and 0.5. As a rule, relatively more substance is adsorbed from dilute solutions or gaseous mixtures than from concentrated solutions.

A quantitative measure for adsorption is the "isotherm" which expresses the quantity adsorbed or is a function of its concentration in the boundary phase. This is the well-known Freundlich adsorption isotherm. This adsorption curve indicates that with an increasing concentration of the adsorbed substance  $c$  in one phase, solution or gas, there is an increase in the amount  $a$  adsorbed following the so-called "exponential" function,  $a = \alpha C^{1/n}$ , where  $\alpha$  and  $n$  are constants;  $C$ , the concentration of the solution

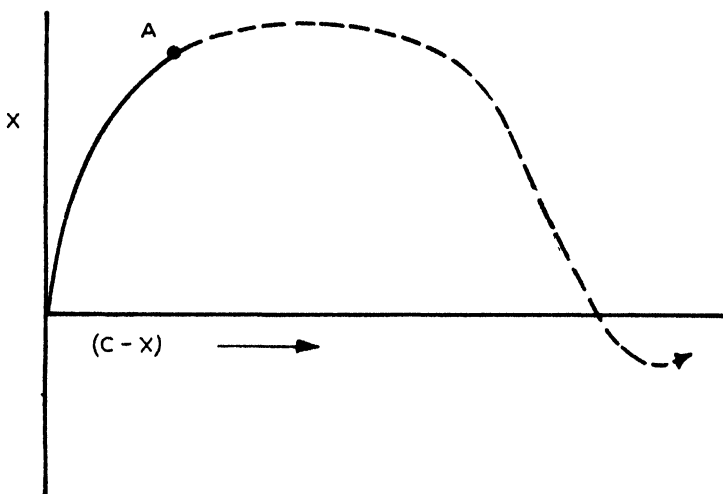


FIGURE 3.

in moles per liter; and  $a$ , the adsorbed amount expressed in milli-moles per gram. Adsorption isotherms of lower fatty acids on charcoal are illustrated, according to Freundlich, in Fig. 2.

If  $x$  is the amount adsorbed from a unit volume of solution having an initial concentration  $C$ , then  $C - x$  is the equilibrium concentration and the curve for the adsorption, Fig. 3, follows the equation:  $x = K(C - x)^n$ . The curve in Fig. 3 shows that for smaller concentrations relatively larger amounts are adsorbed than for higher concentrations. Adsorption reaches a maximum at a definite saturation concentration and decreases with a further increase in concentration. Fig. 4 is a general expression for the adsorption curve.

Physical conditions influence adsorption. It is generally known that adsorption increases with a decrease in temperature, but there are cases in which adsorption increases with an increase in temperature. The temperature coefficient is rather small. Two kinds of dependence on temperature

must be taken into account: (a) by maintaining constant pressure and comparing the amounts adsorbed at different temperatures, curves are obtained which are called "isobars";<sup>36</sup> (b) by maintaining the amount adsorbed constant and comparing the pressures at different temperatures, curves are obtained which are called "isosteres."

The constant  $K$  of the foregoing equation is a measure of the extent of adsorption and varies considerably for single adsorbents. To determine the value of  $K$ , as well as  $n$ , the logarithmic expression for the equation:  $x = K(c - x)^n$ , which is  $\log x = n \log (c - x) + \log K$ , was used. As shown in Fig. 4, the equation corresponds to a straight line, and the tangent of angle  $\alpha$  is equal to  $n$ . The coefficient  $K$  of the adsorption formula in

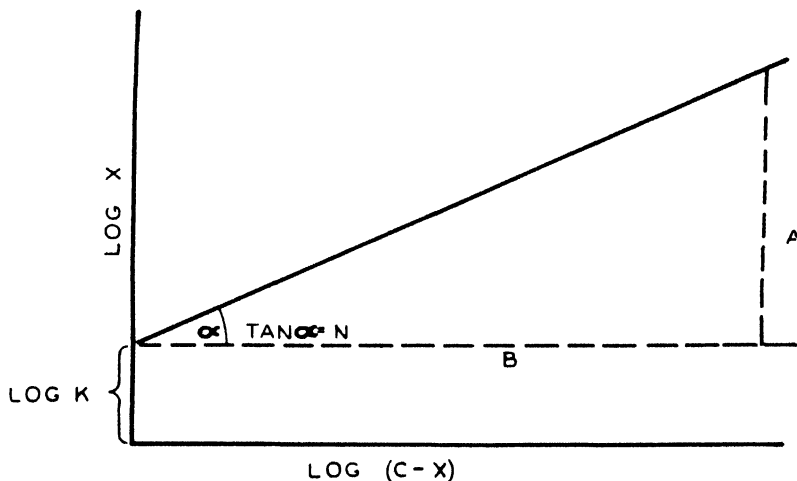


FIGURE 4.

general is found to be smaller for organic solvents, such as alcohol, ether, benzene and acetone than for water; therefore, a substance adsorbed from water may be displaced from the adsorbent with an organic solvent.

The relationship between pressure and the extent of adsorption (corresponding to the concentration) of a gaseous adsorbate at a constant temperature is frequently expressed by the equation:  $\frac{x}{m} = Kp^{1/n}$ , where  $x$  is the amount absorbed by  $m$  grams of the adsorbent;  $K$ , the constant;  $p$ , the pressure of gas, and  $n$  varies from 1 to  $\infty$ .

This equation is applicable to a limited range in pressure; for a larger range in pressure, Langmuir derived an equation based on the principle of surface uniformity and the unimolecular adsorption layer concept:  $\frac{x}{m} = \frac{k'bp}{1 + bp}$ , where  $k'$  and  $b$  are constants (for small pressures,  $n = 1$ ; for large pressures,  $n = \infty$ ).

Adsorption has been found to be proportional to pressure for the range of low pressures and independent of pressure at sufficiently high pressures.

Therefore, the variation in the exponent of pressure with increased adsorption is the criterion of adsorption. The shape of the adsorption isotherm is highly dependent upon the adsorption forces and those of interaction between the adsorbed molecules. Thus  $I_2$  may be considered to adsorb on silica in the molecular form, and that all of the forces are predominantly of the van der Waals' additive type. The forces of this type seem to be much weaker between  $I_2$  and the silica surface, than between the  $I_2$  molecules themselves. Thus the adsorption must rise very slowly for the nearly bare surface ( $Q \sim 0$ ) as the pressure of the  $I_2$  vapor is increased. However, after a considerable portion of the surface is covered, the amount of iodine increases much more rapidly since it is now held not only by the silica surface but by neighboring  $I_2$  molecules. This gives the isotherm the shape exhibited in Fig. 4a.

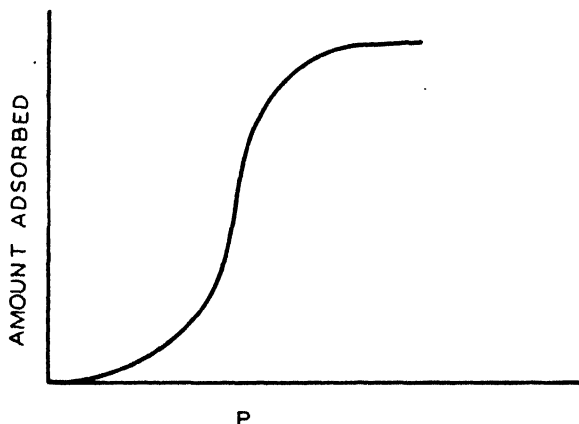


FIGURE 4a.

When the amount adsorbed is very large, the film becomes multi-molecular and finally the vapor pressure becomes constant and equal to that of iodine in bulk.

#### ADSORPTION ISOTHERMS FOR HYDROGEN

The curves have the general form of the Langmuir isotherm:  $x = \frac{abp}{1 + ap}$ , where  $x$  is the amount of gas adsorbed in cubic centimeters per 100 grams of metal, or  $\frac{p}{x} = \frac{p}{b} + \frac{1}{ab}$  ( $p/x$  plotted against  $p$  should give a straight line). In most cases there is a large adsorption at low pressures, which increases rapidly at first and more slowly as the pressure is increased. Sometimes an adsorption at zero pressure is observed, *i.e.*, gas first introduced is completely adsorbed with no increase in pressure. However this should be true only for cases in which the adsorbate is not in the same molecular form in the two equilibrium states, *i.e.*, adsorption of hydrogen by metals wherein the reaction  $H_2 \rightarrow 2H$  is involved. (See Figs. 5, 6, 7, and 8.)

## ADSORPTION ISOTHERMS FOR CARBON MONOXIDE

Taylor and Williamson,<sup>51b</sup> studying the adsorption of hydrogen on a manganous oxide-chromic oxide catalyst at 165 mm. pressure, obtained

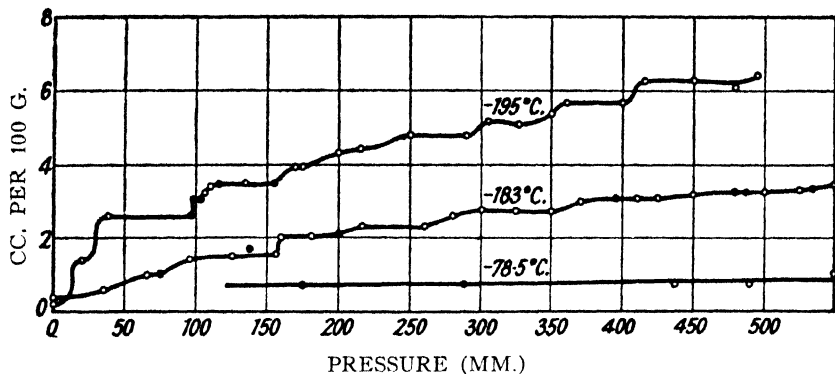


FIGURE 5.—Adsorption Isotherms for Hydrogen on Iron Reduced at 450° (Benton<sup>48</sup>).

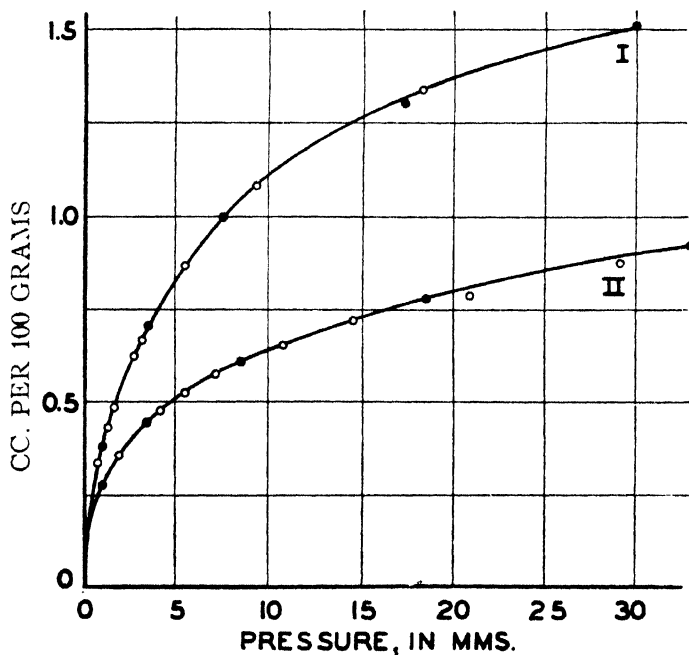


FIGURE 6.—Adsorption Isotherms for Hydrogen on Copper Powder at 25°.

two isobars as shown in Fig. 11, which clearly indicates two adsorption processes with an intermediate range, where both occur. Due to the low temperature activated adsorption does not reach equilibrium in a measurable time. Similar isobars were found for the adsorption of gases by metals.

Taylor and McKinney<sup>61a</sup> obtained evidence for the existence of two types of adsorption processes also in the case of adsorption of carbon monoxide by palladium at 150 mm. pressure as indicated in Fig. 12.

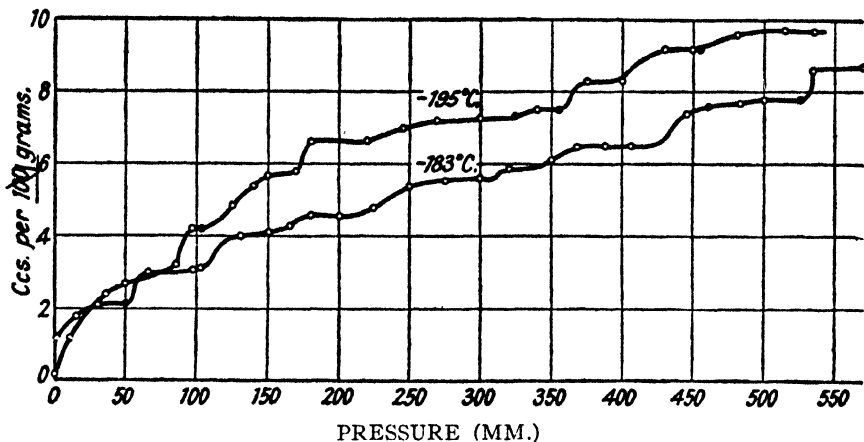


FIGURE 7.—Adsorption of Hydrogen on Copper Reduced at 140° (Benton<sup>4a</sup>).

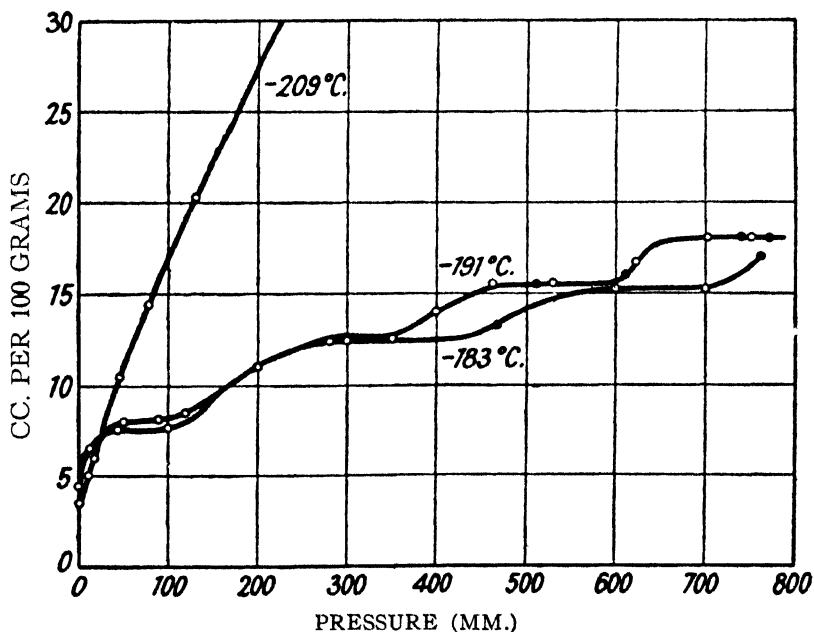


FIGURE 8.—Adsorption of Hydrogen on Reduced Nickel (Benton and White<sup>4b</sup>).

Many equations for adsorption have been derived by a number of investigators and may be classified as those: (a) for different adsorbents; (b) for a variety of adsorbates, and (c) for adsorption processes of varying nature, such as chemical, distributive, and capillary.<sup>37</sup>

Adsorbents differ in regard to the nature of their surface and may be



one of the following: (a) with a plane surface having only one kind of space lattice; (b) with a plane surface having more than one kind of elementary space; (c) with an amorphous surface in which all elementary spaces may be unlike; (d) with a surface in which each elementary space contains more than one adsorbed molecule; (e) with a surface in which the elementary spaces are occupied by single atoms of the adsorbate, and (f) with a surface having an adsorbed film more than one molecule thick.<sup>25</sup>

A distinction may be made in adsorption processes according to whether they proceed from a liquid (solution) or from a gas (vapor) phase. deSaussure<sup>44</sup> was the first to formulate an equation for the adsorption of gases. Bergter<sup>6</sup> derived two equations for the adsorption of gases, one of which was of the exponential type. deSaussure's equation for gases was extended by Boedeker (1859)<sup>8</sup> to adsorption from solutions. Mills and Thomson<sup>33</sup> and Mills and Takamine<sup>32</sup> first proposed an equation for:

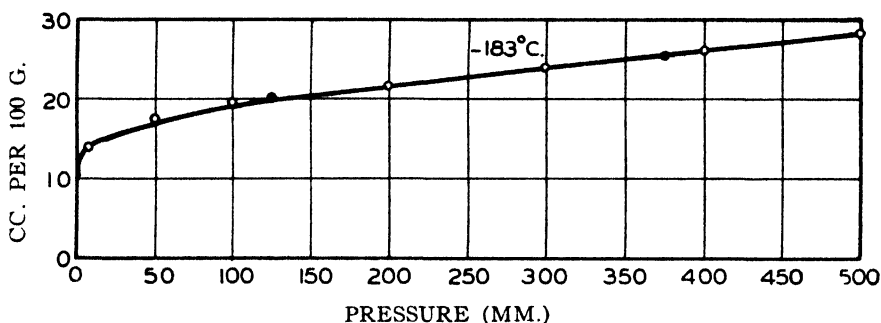


FIGURE 9.—Adsorption of Carbon Monoxide at  $-183^{\circ}$  on Iron Reduced at  $450^{\circ}$  (Benton<sup>4a</sup>).

(a) the rate of adsorption, and (b) adsorption from solutions on fibers. Kroecker<sup>24</sup> and Freundlich<sup>12</sup> deduced, from a series of experiments, an equation for adsorption from a solution. Zacharias<sup>54</sup> and many others formulated equations for determining the rate of adsorption from a solution. Pickles<sup>38</sup> attempted to apply the same equation for adsorption from a gas to adsorption from a liquid. Schmidt and Hinteler<sup>48</sup> and McGavock and Patrick<sup>30</sup> formulated equations for adsorption in which the adsorbate was an organic vapor.

The rate of adsorption in the above equations has been considered as a function of time required for the attainment of an equilibrium in the adsorption system. Marc<sup>28</sup> interpreted the rate of adsorption by assuming that it is a function of the attractive force, the osmotic pressure of the solute, and the kinetic energy of the adsorbed molecules. Gustave<sup>18</sup> modified the adsorption equation to one in which the rate of adsorption is proportional to the free surface and the total amount of the adsorbate in a gaseous or liquid phase.

Frequently the same type of adsorption ability has been found for many substances. However, the specific character of adsorption has not been well defined for certain substances as, for example, the adsorbent charcoal. Many dissolved substances show a wide range in their ability

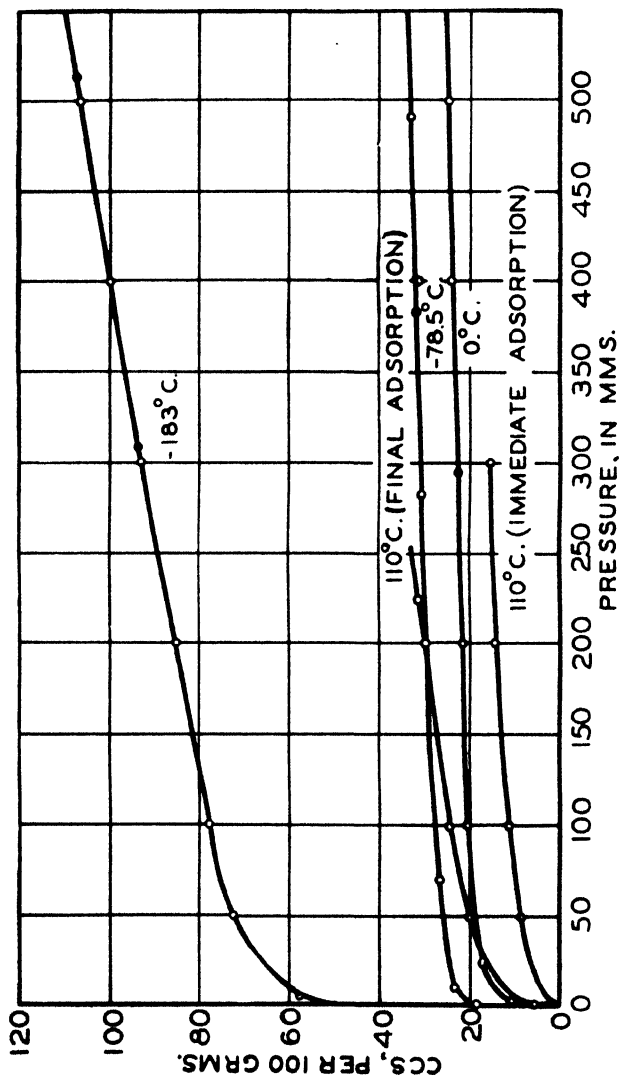


FIGURE 10.—Adsorption of Carbon Monoxide on Copper Reduced at 140° (Benton 4\*).

to be adsorbed which may be regarded as a function of a relationship existing between the dissolved substance and the solvent. The factor of surface activity is of great importance when dealing with the adsorption

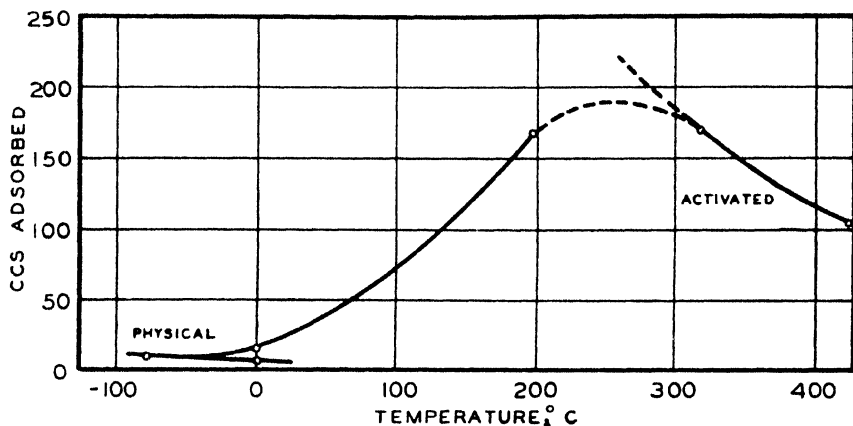


FIGURE 11.—Isobar for Hydrogen on a Manganese Oxide-Chromic Oxide Catalyst at 165 mm. Pressure (Taylor and Williamson<sup>61c</sup>).

of dissolved substances. As a matter of fact, solutions of surface-active substances are in general well adsorbed at the boundary solid/liquid,

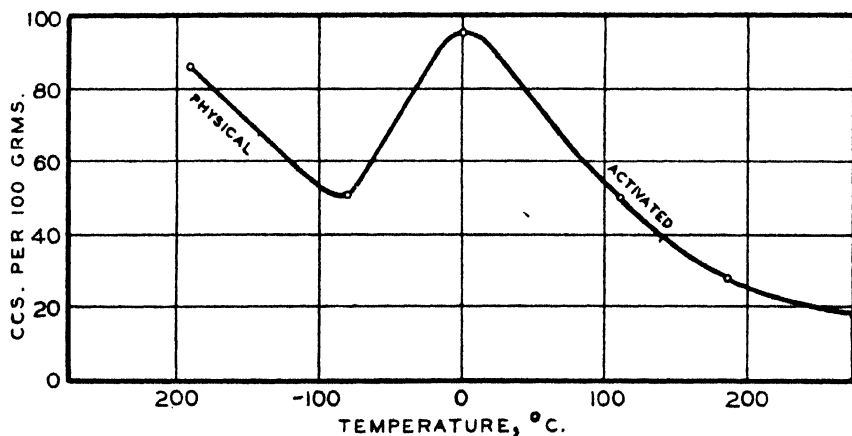


FIGURE 12.—Isobar for Carbon Monoxide on Palladium at 150 mm. Pressure (Taylor and McKinney<sup>61a</sup>).

while surface-inactive substances dissolved in organic solvents are not readily adsorbed. On the other hand, substances not affecting the surface tension of the solvent may be well adsorbed. Charcoal is such an adsorbent for organic acids, sugars, dyestuffs and alkaloids. The initial adsorbability

for surface-active substances at the boundary solid/liquid may be changed in the event another substance has been added or was originally present. Adsorption from mixtures of two substances is specific for each pair of substances and is not directly related to relative dissociation. There may be a mutual increase in adsorption by both substances and there may be a change in the degree of adsorption of one substance in the presence of another substance which is not readily adsorbed such as, for example, the action of neutral salts upon the adsorption of acids and bases and other salts having common ions. The mutual influence of substances on their ability to be adsorbed may be attributed in the case of liquid phase to a change in the number of mols, or to the formation of solvated molecules. Adsorption from mixed solvents is dependent on the character of that mixture. There is a minimum for a definite composition, and it has been proved that mixtures of two solvents have an adsorption corresponding to both pure solvents.

Concerning the nature of electrolytes in adsorption, it is known that acids and bases are more readily adsorbed than salts. It has also been found that compounds having the same cations and the same anions are specific and regular with respect to their adsorbability.

Shilow and his co-workers<sup>46</sup> have proved experimentally that compounds with different cations and the same anions are arranged in groups according to the valency of the cations. Compounds with the same cations and different anions are arranged in groups according to those containing similar types of compounds, such as, for example,  $H_3XO_3 \longrightarrow H_3XO_4 \longrightarrow H_2XO_4 \longrightarrow HXO_3 \longrightarrow HXO_4$ . Each representative group of compounds is influenced by the atomic weight of the cation and anion, respectively, and their relation to the periodic system of the chemical elements. The position of the hydrogen atom is another factor responsible for the division of the entire series into two groups, namely, noble metals and base materials (the covalent and antivalent series).

The problem of the adsorption of electrolytes has been found rather difficult to interpret in many cases, particularly when the nature of the adsorbate or adsorbent was considered responsible for the phenomenon of adsorption. Shilow and his co-workers<sup>46, 47</sup> compared adsorption processes of electrolytes on active carbon to a chemical reaction, while Frumkin<sup>14</sup> conceived adsorption on active carbon as a phenomenon electrochemical in nature. According to Shilow and his co-workers, the mechanism of the adsorption process, using charcoal as the adsorbent in contact with air and an electrolyte as the adsorbate may be described as follows. The surface of a gas-free charcoal, activated at a moderate temperature (550°), when exposed to air for a short time, is converted into two basic carbon oxides, *A* and *B*, and an acid oxide, *C*. The carbon is oxidized by oxygen to carbon monoxide with continuous formation and decomposition of oxide *B*, Fig. 13. If carbon is activated with carbon dioxide, the adsorption process differs, Fig. 14; not only are carbon atoms split off as carbon monoxide, but new "active" carbon atoms are formed.<sup>46</sup>

## CATALYSIS

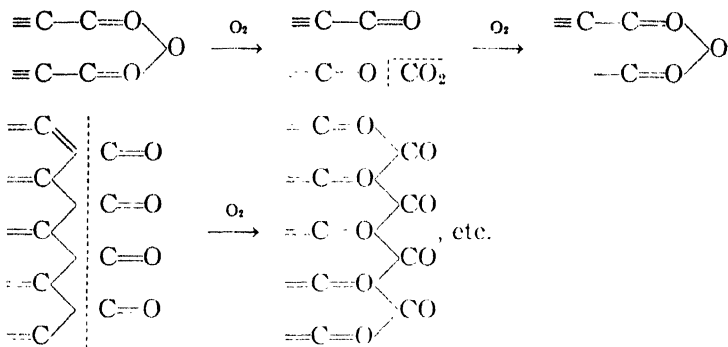


FIGURE 13.

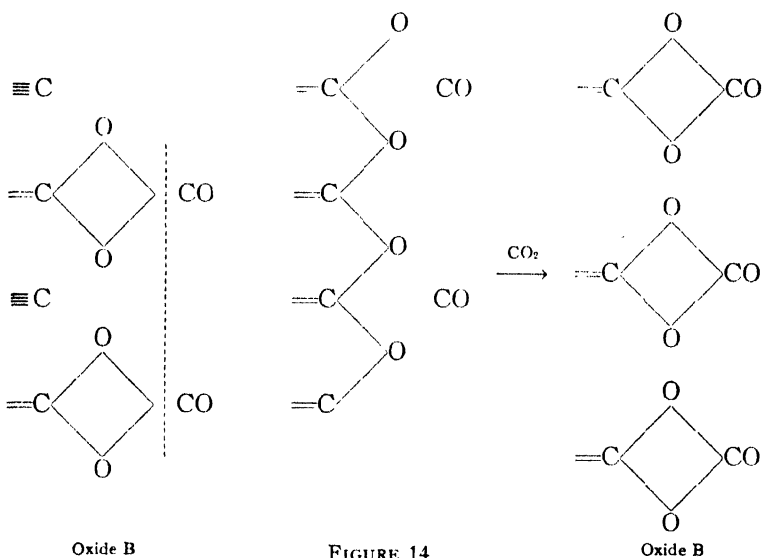
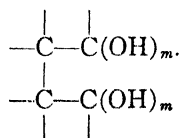


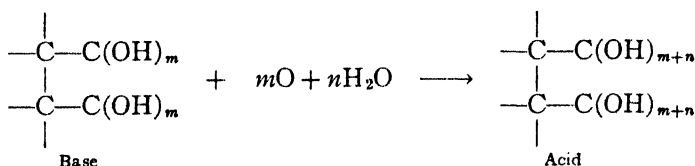
FIGURE 14.

The primary oxide of the carbon surface reacts with water (aqueous solution of the electrolyte) forming a "carbon hydroxide":



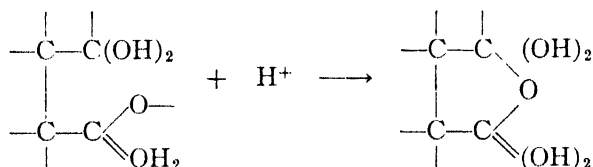
The carbon surface becomes electrically charged through the formation of the oxide, enabling the hydroxide to adsorb definite amounts of molecular oxygen. This carbon hydroxide forms hydroxyl ions. Acids, not alkalies, are adsorbed by the carbon surface charged with hydroxyl ions.

The secondary oxide is an acid oxide forming with water the polyhydroxide compounds which are similar to *ortho*-acids:



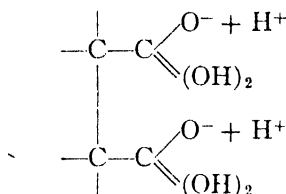
Adsorption of alkalis occurs under conditions determined by three states of the charcoal schematically expressed as follows:

Scheme I:



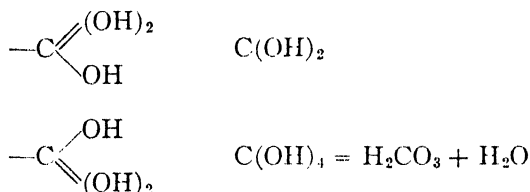
Scheme I corresponds to the formation of an anhydrous oxide.

Scheme II:



Scheme II corresponds to a surface saturation by hydroxyl groups.

Scheme III:

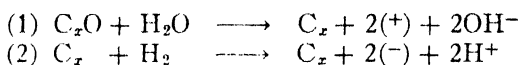


Scheme III corresponds to an autoxidation and reduction or further oxidation by oxygen whereby carbon dioxide is split off.

In the first state, charcoal is stable to alkalis; in the second, charcoal acts as an acid in the presence of alkalis which it neutralizes, resulting in their adsorption; in the third, carbon dioxide is split off from the surface of the charcoal, reacts with the alkali and forms a carbonate, adsorption taking place. Shilow and his co-workers<sup>46</sup> explained in such a way all alkali as well as acid adsorption processes by assuming the formation of hydroxyl groups on the surface of the charcoal, and determined the basic or acidic nature of the oxide by the number of hydroxyl groups on each carbon atom.

Frumkin<sup>14</sup> interpreted the mechanism of adsorption processes on active charcoal by considering charcoal as a gas electrode. From the layer of adsorbed gases the electrode discharging ions into the solution, is charged

itself, and attracts ions of an opposite sign. Oxygenated charcoal also forms hydroxyl ions from the adsorbed oxygen which pass into solution, leaving a positive charge upon the surface of the charcoal. In an acid solution the  $\text{OH}^-$  ions combine with the  $\text{H}^+$  ions of the solution, while the positively charged surface attracts the anions of the solution; therefore the acid is adsorbed from the solution. In adsorption from a neutral solution, the anions of the solution are replaced by the  $\text{OH}^-$  ions, rendering it alkaline. Adsorption from an alkaline solution by oxygenated charcoal is extremely small; alkali, not acid, is adsorbed. When oxygenated charcoal is heated for a time in atmospheric hydrogen, a change takes place, the charcoal discharging  $\text{H}^+$  ions into the solution at the expense of the adsorbed hydrogen but it itself retaining a negative charge which attracts the positive ions from the solution, providing the solution is an air-free electrolyte. Schematically, Frumkin expressed the mechanism of the adsorption of acids (1) and alkalies (2) as follows:



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### CONTACT CATALYSIS

Chemical reactions at boundaries may occur after adsorption takes place. For example, organic acids adsorbed on carbon may be oxidized on it. Decomposition of hydrogen peroxide on glass wool on which salts of heavy metals have been adsorbed shows a decided increase in velocity in comparison to pure glass wool. In this case, the glass wool acts as a carrier, and the salts of heavy metals as catalysts. Freundlich has shown that in certain cases substances having a high adsorption ability may catalytically accelerate chemical transformations. For example, carbon accelerates esterification of fatty acids and in its presence sodium hydroxide reacts instantaneously with benzoyl chloride. The catalytic action of animal charcoal is directly related to its adsorption ability. The catalyst itself may be an adsorbent for gases, for example, in hydrogenation and oxidation processes. Thus the type of catalytic reactions in which the first stage of the process is adsorption corresponds to adsorption catalysis.

Whether adsorption plays a significant role in catalytic processes was considered by Fusinieri (1825), who related the physical properties of the contact surface to the phenomenon which later was described as catalytic activity. Mitcherlich (1833)<sup>50</sup> introduced the term "contact reactions." In 1834, Faraday<sup>27</sup> noted the remarkable increase in the reaction velocity produced by certain substances and the effect of minute amounts of poison on the accelerated reaction, assuming therefrom that the reactants, such as gases, are adsorbed by the accelerating agents or catalysts. Since that time adsorption has been definitely related to catalysis and discussed from many angles by a group of investigators. Above all, it seemed of importance to determine what type of adsorption is associated with catalytic processes.

Thomson<sup>81</sup> assumed that adsorption catalysis is due to capillarity and therefore a surface phenomenon. Experiments carried out by many investigators contradicted Thomson's assertion by stating that adsorption processes occurring in catalysis were not capillary condensations, as the energy changes resulting thereby are much greater than those in condensation processes and in many cases comparable in amount to the energy of chemical reactions. Thomson refers to a theory of chemical capillarity serving to explain catalysis. According to this theory "If the thickness of the adsorbed layer is  $\delta$  and the amount adsorbed per unit area is  $n$  as stated in Gibbs' equation, then the concentration of the reactants in the layer is  $n/\delta$  corresponding to the active mass of the solute. If liquid solutions are considered, then the concentration of the reactants is greater at the surface of the catalyst than in the interior of the solution; conse-



quently, the velocity of the reaction is greater than it would be if the reactants were adsorbed."

There is an apparent discrepancy in defining physical and chemical adsorption. Since the problem of adsorption in catalytic processes has been related to the mechanism existing between the reactants and the catalytic agent accelerating the reaction, differentiation between chemical and physical combinations of components must be considered. In general, selective chemical adsorption is distinguished from physical and molecular adsorption. Chemical adsorption involves valency forces, while physical adsorption involves van der Waals' forces, they being a function of capillarity and critical constants of gases. A typical van der Waals' adsorption is characterized<sup>77</sup> by taking place at low temperatures, while chemical adsorption is identified by a slow rate of reaction increasing with an increase in temperatures. Since a slow process may involve activated adsorption, solution formation, compound formation, or a combination of any one of these, it is recognized that the rate of adsorption in itself is not a criterion for chemical adsorption catalysis.

It is assumed that in order to identify catalytic adsorption processes and to estimate them quantitatively, a wide range of temperatures must be considered, not only for the rate of adsorption, but also for the corresponding equilibria of the process as well. Benton<sup>12</sup> suggested differentiating "primary" adsorption from "secondary" adsorption because the first occurs with active adsorbents and depends on primary valency forces, whereas the second is characteristic for inert adsorbents and depends on secondary valency forces. The forms of isotherms characteristic for these two types of adsorption differ, two types of isotherms being distinguished in adsorption catalysis: (a) those that start at the zero point of the coordinate system as a straight line or a slightly curved line, indicating that the molecules are adsorbed equally strong or weak on the total surface until by competition with one another they cover the entire surface, and (b) those that start at the zero point of the coordinate system, rise abruptly, bend round suddenly, and continue in a normal path, indicating that a part of the surface adsorbs especially strong a considerable amount of gas and only after its saturation does the remaining part of the surface enter into action.

It is well known that either hydrogen or carbon dioxide is reversibly adsorbed on oxides of Cr, Cu, or Zn, at room temperatures, but at high temperatures they are recovered as water or carbon dioxide.<sup>33a</sup> The adsorption of carbon monoxide on platinum is reversible at liquid air temperature but irreversible at room or high temperatures. The adsorption which occurs in these cases at the lower temperatures is of the physical or van der Waal's type, which resembles closely the condensation of the liquid on its own surface. However, in the case of the adsorption, the energy liberated is much higher if solids of high cohesion are the adsorbents. As in the case of a vapor-liquid system equilibrium is always attained rapidly when the gas and the adsorbing surface are brought into contact and the process of adsorption is completely reversible. In contrast with van der Waals' adsorption, chemical adsorption is often slow, through it,

adsorption is often irreversible. In general, however, the amount of heat liberated is greater, and often much greater.

Taylor proposed for the differentiation between "primary" and "secondary" adsorption the reversibility of the process and the evaluation of its energy. The "secondary" or "reversible" adsorption processes are those normally having small heats of adsorption and small energies of activation, while the "primary" or "irreversible" adsorption processes frequently have high heats of adsorption and moderate or large energies of activation. This latter classification clearly emphasizes the fact that adsorptions with higher activation energies are those of significance in catalytic changes. Therefore, the type of adsorption to be associated with catalytic processes is the "primary" or "irreversible" chemical and activated adsorption. However, in spite of all attempts to define the conception has always been the same, namely, that there exists a wide range of adsorption phenomena differing more or less from the "secondary" physical or "reversible" (van der Waals') molecular type and characterized by greater binding forces, larger heats of adsorption, and increased reactivity of the adsorbed gas. Low-temperature adsorption is instantaneous and occurs without a considerable heat of adsorption (not higher than 0.1 volt). At higher temperatures, adsorption occurs with increasing velocity. The activation energy of the high-temperature adsorption may be calculated from velocities obtained at various temperatures. Taylor termed this adsorption "activated adsorption." The heat of adsorption in activated adsorption is higher (exceeds 0.9 volt) than in low-temperature adsorption.

Contrary to van der Waals' adsorption, activated adsorption is assumed (Nyrop) to be due to an ionization which sets in at the catalyst surface only above a certain temperature. Thus the minimum temperature at which activated adsorption begins is its characteristic feature.

#### Activated Adsorption

Gas	Catalyst: Metal	Temperature	Observer
H <sub>2</sub>	Ni	(traceable) 83° K.	White
H <sub>2</sub>	Ni	-145° C. and -118° C.	Leypunsky: <i>Acta physicochim. U.S.S.R.</i> , <b>5</b> , 807-812 (1936).
H <sub>2</sub>	Pt	195° K.	White.
H <sub>2</sub>	Fe	90-195° K.	Benton: <i>Trans. Far. Soc.</i> , <b>28</b> , 202 (1932).
H <sub>2</sub>	Ag	470° K.	Drake and Benton: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 506 (1934).
H <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub> gel	195-491° K. (0.125-1.0 atm.)	Buswell, Jr. and Taylor (H. S.): <i>J. Am. Chem. Soc.</i> , <b>58</b> , 697-705 (1936); 1753-1755 (1936).
H <sub>2</sub>	ZnO		
N <sub>2</sub>	W	293° K.	Frankenburger and Hodler: <i>Trans. Far. Soc.</i> , <b>28</b> , 234 (1932).
N <sub>2</sub>	Fe	273° K.	Benton: <i>Ibid.</i> , <b>28</b> , 202 (1932).
N <sub>2</sub>	Ni	98-173° K.	Benton and White: <i>J. Am. Chem. Soc.</i> , <b>52</b> , 2325 (1930).
CO	Cu	273° K.	Taylor and Strother: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 506 (1934).
CO	Fe	195° K.	

In case of adsorption of a gas<sup>28</sup> on a hot surface (a typical elementary case of adsorption catalysis), various types of adsorption may be inferred, ranging from a purely physical, electrically neutral adsorption or condensation up to the formation of a definite stable chemical compound likewise electrically neutral. Dubinin,<sup>23</sup> discussing capillary condensation of vapors on porous solids, states that for solid adsorbents with coarse pores adsorption is largely a capillary condensation, while for fine pores Polanyi's adsorption theory is applicable; for intermediate cases, both adsorption and capillary condensation exist together.

When the catalytic and the adsorption phenomena are combined, the catalyst which is an adsorbent effects a chemical reaction. It is assumed that the mechanism of this type of catalysis is expressed either in the formation of intermediate compounds between the catalyst and the reacting substance or, under the influence of valence forces of the catalyst, whether it adsorbs little or none of the reacting substances, a loosening and weakening of valence forces between the atoms of the reacting substance takes place which may lead to isomerization, polymerization, depolymerization of the substance, or to a splitting of the molecules with separation of active shreds.<sup>82</sup>

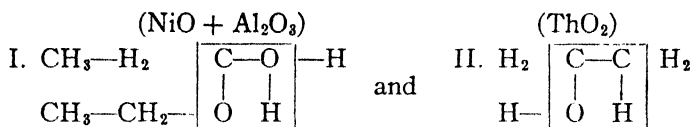
A chemical reaction proceeds more readily the looser the binding which must be set free during its course. Polanyi<sup>61</sup> designated heterogeneous catalysis as "adsorption catalysis" when it was caused directly by the adsorption action of the catalyzing wall. He emphasized that pure adsorption catalysis excludes not only those cases in which the catalyst combines chemically with a reacting substance, but also catalysis of the type occurring in reactions of hydrogen or oxygen on metallic surfaces because these gases are adsorbed abnormally on metals.

Bancroft,<sup>9</sup> in his theory of "contact catalysis" differentiated two types of adsorption catalysis: (a) that in which the mechanism lies in the formation of definite chemical compounds, and (b) that in which the mechanism is related to adsorption with activation. The second mechanism is a prerequisite for the reaction in which the catalyst converts the reacting substances into active modifications and, as the adsorbed substances are held by bonds at the adsorbent-catalyst, the latter causes the opening and closing of these bonds or contravalences. Which bonds are opened depends on the particular catalytic process. For example, acetic acid adsorbed by charcoal may attach itself [reaction preceded by dissociation (Neff)]: (a) by the methyl carbon; (b) by the carboxyl carbon, or (c) by either of the oxygens. It may also attach itself by any of the hydrogens [reaction preceded by association (Michael)].

With respect to identifying the formation of intermediate compounds, Bancroft remarks that although their presence does not always account for the catalytic action, nevertheless it is necessary to look for them. As definite evidence of intermediate compound formation in "contact catalysis," the catalysis of hydrogen peroxide with mercury as catalyst may be cited as an example, the mercuric peroxide being the intermediate compound detected as a film intermittently formed.<sup>14</sup>

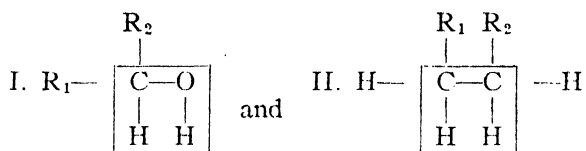
Balandin<sup>7</sup> interprets the mechanism of adsorption catalysis from the

viewpoint of his multiplet hypothesis. Not only the reacting substance, for example, water in hydration processes, but other components of the system, namely, shreds or part of molecules, exercise their influence in adsorption catalysis. If those atoms of the reacting molecules are considered in which during reactions I (hydration of ether or the olefins) and II (dehydration of alcohols to olefins) a change in valence bonds takes place, then two schemes differing in chemical nature of the reacting parts of the molecules are obtained:



The difference between these two schemes is the substitution of a carbon atom in Scheme II for an oxygen atom in Scheme I. The chemical nature of forces acting between catalyst and the reacting substances differs, therefore catalysts for both reactions should not be of the same character.

Balandin gives another example of this mechanism in dehydrogenation reactions of alcohols and aromatic hydrocarbons:



Copper, for example, is more suitable for the dehydrogenation of alcohols (I), while platinum<sup>91</sup> dehydrogenates more readily the hexahydroaromatic hydrocarbons (II). Balandin's hypothesis is not in agreement with Taylor's<sup>76</sup> conception of the mechanism of adsorption catalysis in which the metal oxides serve as binary catalysts, for in this reaction the reacting molecule is adsorbed by only one type of ions of the catalyst and, depending whether it is adsorbed on the positive metal ion or on the negative oxygen ion will determine whether a dehydrogenation or a dehydration process takes place. Taylor applied his interpretation to alcohols and acids.

In connection with Taylor's theory, it is interesting to note that Bayliss,<sup>11</sup> in his experiments on the adsorption of electropositive and electronegative dyestuffs on filter paper with special reference to the action of electrolytes, found an unusual result in the amount of dye adsorbed in a given period of time by the addition of small amounts of neutral salts, namely, in electronegative dyes the cations of electrolytes promote adsorption, while the anions retard it; in electropositive dyes, the cations retard adsorption, while the anions promote it. In a neutral salt, the effect of the cation is predominant and, when added to electronegative dyes, its addition always promotes adsorption. Harker<sup>37</sup> extended these experiments to a study of the effect of  $\gamma$ -rays (radiated from radium needles) on adsorption from aqueous solutions of dyestuffs (congo red and methylene blue) and found that adsorption was retarded more with methylene blue (electropositive) than with congo red (electro-

negative). In the presence of electrolytes, the action of the  $\gamma$ -rays was modified, *i.e.*, the retardation of adsorption increased for congo red and decreased for methylene blue, both of which were in agreement with Bayliss' results.

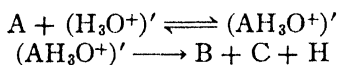
There are other interpretations of the mechanism of adsorption catalysis. It is a recognized fact that when metal catalysts are used a surface phenomenon, apparently chemical in nature but in all probability including a rearrangement of electrons in both the adsorbent and the gas, may be involved. Thomson<sup>82</sup> assumed that the molecules of hydrogen and oxygen combine under the action of a glowing platinum wire or a carbon filament (heat induced by an electric current) due to a stream of electrons. This is made especially clear by the action of x-rays on the reaction because, under these conditions, the molecules of hydrogen and oxygen combine even in the cold under the influence of discharged electrons. Nyrop,<sup>55</sup> studying the catalytic effect of a catalyst which adsorbed x-rays or  $\gamma$ -rays, assumed that these radiations acted by displacing electrons from atoms, modifying both adsorption and catalytic processes in the sense of improving them. As an illustration, Nyrop mentioned the fact that catalyst palladium or copper was stimulated by x-rays due to the rapidly moving electrons on the surface of the catalyst.

Nyrop<sup>55a</sup> considered activated adsorption and catalysis as two parallel phenomena, both produced by the ability of surfaces to cause ionization. The conditions postulated for a catalytic reaction on an active surface are the same as those in electronic bombardment reactions, namely, the ability of the surface to cause ionization, and the energy of the bombarding electrons must be greater than the ionization potential of molecules of the reactants most difficult to ionize. As in the electronic bombardment reactions, a slowing down of the reaction takes place when molecules of a low ionization potential are present, likewise in catalytic reactions molecules with a low energy of ionization act as poisons. The catalytic action of the surface depends on the maximum kinetic energy of free electrons of the catalyst. The apparent energy of activation of a reaction is lowered by the intermittent ionization produced by the catalyst and the velocity of the reaction in its turn is increased by the lowered energy of activation. Thus catalysts with high ionization ability should require the lowest amount of activation energy. Activation energies in dehydrogenation processes with respect to various catalysts have been measured by Balandin<sup>6a</sup>

Hydrocarbon	Catalyst	<i>E</i> in K <sub>g</sub> ./cal.
Piperidine.	Pd	16.2
	Pt	19.9
Decahydronaphthalene.	Ni	<10.0
	Os	10.0
	Os	16.5
	Pt	19.0
Cyclohexane.	Ni	9.7
	Ni	13.7
	Pd	15.3
	Pt	18.0

who found that the catalytic ability decreases from nickel to platinum. Assuming that a catalytic reaction takes place only if an electron is moved from substances with a low energy of ionization to substances with a high energy of ionization and then to the catalyst and that the change in reactivity occurs only when the energy gained in neutralizing the ion is larger than the ionization potential of the reacting molecule, only under this condition is the transfer of an electron from the molecule to the ion possible and the reaction accelerated.

Nyrop attempted to produce experimental evidence for this reaction mechanism on catalytic surfaces. If a hydrogen ion ( $H^+$ ), *i.e.*, a proton collides with a molecule having an ionization potential less than 13.54, an electron will be transferred from the molecule to the ion. For instance, water with an ionization potential of 12.9 volts forms on colliding with a proton the ion  $(H_3O^+)'$ . This ion may react in turn with molecule A of a low energy of ionization and the reaction taking place is said to be:

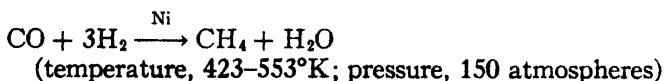


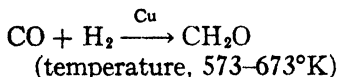
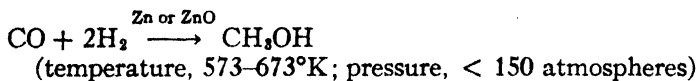
in which  $(AH_3O^+)'$  is an intermediate fugitive complex subsequently decomposed. The proton furthers the reaction  $A + H_2O \longrightarrow B + C$  and any substance able to produce the proton is the catalyst.

In order to determine whether the catalyst is suitable for a hydrogenation reaction, not only is it necessary to know whether the surface ability to cause ionization is about the same as the ionization energy of hydrogen, but also how the ionization ranks with respect to that of the inorganic or organic compounds to be catalyzed. Considering the energies of ionization of organic compounds:

Compound	Volts
Methane.	13.7
Ethylene.	11.5
Acetylene.	12.3
Benzene.	9.6
Carbon monoxide.	15.0
Carbon dioxide.	14.3
Hydrocyanic acid.	14.8

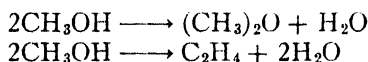
as well as the energy of hydrogen ionization which equals 15.37 volts, it is plausible that surfaces able to ionize hydrogen will be able to ionize the above organic compounds. Therefore hydrogenation may be carried out successfully using catalysts whose ionization energy is above or at least equal to 15.37 volts. The ionization energy of osmium, molybdenum, tungsten, iron, nickel and manganese is greater than 16.7 volts; that of mercury, less than 15.37 volts, and that of copper, slightly above 15.37 volts. The choice of a catalyst may also determine the reaction products of the reaction:





If the ability of copper to cause ionization is about equal to that of hydrogen, then hydrogen molecules adsorbed on copper will be surrounded by carbon monoxide molecules, and in all probability formaldehyde will form. On a zinc catalyst the adsorption of hydrogen is relatively greater than that of carbon monoxide, while on a nickel catalyst the adsorption of hydrogen is especially strong, favoring the formation of methane. If the catalytic surface has certain patches in the surface which are able to ionize products having a lower energy of ionization than that of hydrogen, compounds different from those normally obtained are produced on these less active parts.

If chromium is added to a zinc catalyst there are obtained, in addition to methanol, ether and ethylene:



Therefore methanol is adsorbed on the zinc-chromium catalyst. Likewise, copper decomposes methanol into methyl formate, and the addition of zinc oxide to the copper catalyst alters part of the products of decomposition to formaldehyde, carbon monoxide and hydrogen. The alteration increases with an increase in the amount of zinc oxide.

Roginsky,<sup>66</sup> discussing the mechanism of adsorption catalysis, developed a scheme of catalysis based on the concept of a deformation of molecules on the surface as the primary and fundamental process of catalysis. If this scheme is applicable, then a classification of catalytic reactions should be possible according to the deformation type, such as catalysis through a "virtuel" valence.

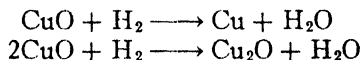
Freundlich interpreted the catalytic action resulting from adsorption on carbon by the action of surface energy, depending on the degree of dispersion of the carbon. Rusznyak<sup>68</sup> investigated and studied the influence of surface energy in the catalytic decomposition of hydrogen peroxide by gold salts of varying degrees of dispersion; he found that, although the degree of dispersion of the catalyst changes the reaction velocity, there is no strict proportionality for its function.

It appears that an explanation for the mechanism of adsorption catalysis is even more difficult than that for adsorption processes. Ordinary adsorption and catalytic adsorption are unlike in function. Catalytic adsorption involves more than an increase in concentration at the surface, for it is assumed that catalytic reactions proceed in adsorption layers of comparatively high concentration.<sup>48</sup> The catalytic action of one and the same adsorbent does not always proceed in the same direction. Kruyt and van Duin<sup>44</sup> pointed out that charcoal retarded the saponification of

ethyl acetate and sodium methyl benzoate-*p*-sulfonate, while it accelerated debromination of  $\alpha$ - $\beta$ -dibromopropionic acid, using potassium iodide.

Bancroft<sup>9</sup> interpreted negative catalysis by attributing it to an anomalous orientation of molecules which may occur when two reacting substances more or less polar are adsorbed in such a manner that the reacting portions are turned away from each other. Ipatieff<sup>38</sup> attempted to explain the catalytic dehydration property of alumina by its ability to combine with water, liberating heat and giving off water under definite physical conditions, particularly temperature. The double reaction proceeds at a great rate of speed and for this alumina must be in a state of maximum adsorption. Recently, Guichard<sup>34</sup> opposed the viewpoint that in the case of alcohol dehydration on aluminum oxide the formed water is almost wholly adsorbed on the catalyst by stating that it involves rather a bivalent adsorption mechanism whereby the preferred adsorption of alcohol molecules favors the acceleration of the reactions through aluminum oxide. He obtained isothermal and isobar adsorption curves for alcohol, ether and water vapor on aluminum oxide and by extrapolation of these measurements from ordinary temperatures to 240° the results obtained indicated that at this temperature practically no adsorption of ether and water took place and this was at the moment when half of the alcohol was converted into ether and water. Ipatieff favors the viewpoint of Faraday, Thompson and Langmuir who assume the existence of thin adsorbed films on the surface of the catalyst which behaves very specifically and makes the catalytic adsorption a function of co-action of physical and chemical factors. This conception cannot be reverted because adsorbents which are very similar in their physicochemical properties do not produce identical catalytic effects.

Equally good adsorbents are not necessarily equally effective catalysts for one and the same reaction. Silica and alumina are both good adsorbents, adsorbing almost equal amounts of water, yet behaving differently with respect to the dehydration of alcohols. On the other hand, there are cases in which the catalytic inactivity of a substance has been attributed to a lack of adsorbing power of the catalyst for the reacting component of the system. Palmer<sup>56</sup> emphasized the fact that metallic copper as a catalyst for the decomposition of alcohol obtained by reduction may vary in its activity depending upon the relationship between the velocity curves for these two reactions:



In agreement with Rideal's observations that copper prepared by reduction of cuprous oxide is more readily attacked by ordinary reagents than copper originating from cupric oxide, Palmer postulated that copper from cuprous oxide is a more active catalyst than copper from cupric oxide and interpreted the inactivity of "cupric" copper in the decomposition catalysis of alcohol by lack in the adsorption ability for alcohol.

Both adsorption and catalytic activity differ and are specific not only for chemically and physically different groups of adsorbents, such as



metals and inert substances, but also within one and the same group the efficiency with regard to adsorbability and catalytic activity depends on the state, sub-division (aggregate, massive, sponge) and condition of the corresponding surface, (bright or dull). Difficulties encountered in reproducing catalysts of a definite degree of activity are due, in all probability, to neglect in considering factors pertinent to the original status of a catalyst. As an illustration, mention may be made of platinum black, platinum sponge and massive platinum used in the oxidation of ammonia.<sup>60</sup> Massive platinum with a bright surface was found to have almost no catalytic activity; platinum black and platinum sponge were active to such an extent that oxidation proceeded to nitrogen and water vapor. Therefore, a type of platinum other than the three discussed was assumed to be effective in oxidizing to nitric oxide. Now, bright wire gauzes were inactive, but as soon as the surface was dulled by pretreating with a mixture of ammonia and air, the catalytic activity improved.

In uniting hydrogen and oxygen catalytically, porcelain chips were used as catalyst which had both a stimulating and a retarding action on the rate  $K$  at which hydrogen and oxygen combined to form water. Porcelain chips pretreated with oxygen for 24 hours reduced the rate  $K$  from 0.0430 normal to 0.0305, while hydrogen effected an increase in  $K$  from 0.0430 to 0.0515 in 24 hours and to 0.0622 in 72 hours. Magnus and Cahn<sup>49</sup> attempted to draw a relationship between adsorption catalysis and the influence of pretreatment of the adsorbent upon gas adsorption; adsorption of carbon dioxide, nitrogen, and ethylene on silica gel.

Rideal and Thomas<sup>54</sup> compared the adsorption of methylene blue from aqueous solutions by three types of fuller's earth (Florida, Surrey and Somerset), as well as their adsorption and catalytic activities in the decomposition of hydrogen peroxide. They found that while adsorption was approximately proportional to the specific surfaces of the earths, their catalytic activity in decomposing hydrogen peroxide was independent of their ability to adsorb. Rideal and Thomas obtained different adsorption values for the three earths, but were unable to correlate them with the surface extension. They concluded that the governing factor in catalysis may be due to the presence of a specific oxidate. The following table shows the relationship between the iron present in the earth and the amount of water adsorbed.

Earth	Water Adsorbed %	Iron as $\text{Fe}_2\text{O}_3$ %
Florida.	7.64	6.98
Surrey.	14.25	6.40
Somerset.	12.32	3.15

In the case of Somerset earth, the iron content was in excess of that anticipated from catalytic activity, but its velocity coefficient showed a continuous increase in value, indicating an increase in activity on the part of the iron.

Alexejewski and Golbraich,<sup>48</sup> studying the sorption and catalytic properties of active manganese dioxide (prepared by the conversion of potassium permanganate with manganese sulfate) with respect to

organic compounds such as isobutyl and isopropyl alcohols, propionic and acetic acids, xylene, toluene, benzene, chlorobenzene, aniline, etc., in a vapor state, showed that the course of the reactions may vary from pure adsorption to chemisorption through to catalysis.

The least adsorption was found for benzene and carbon tetrachloride and explained by the apolarity of both compounds. The adsorption isotherm for carbon tetrachloride and chlorobenzene showed sharp breaks, indicating the beginning of a capillary condensation. Adsorption of aniline was accompanied by oxidation to azobenzene. Analogous to aniline, benzonitrile was converted by sorption through manganese dioxide into benzamide. The adsorption of dry ammonia on manganese dioxide (a normal adsorption) was found to take place at 0°. By raising the temperature above 50°, the chemisorptive character of the reaction was made evident whereby ammonia was oxidized to nitrogen and water.

Poljakow, Neumark and Malkin<sup>61a</sup> deduced from a graphical presentation of isotherms of the adsorption of benzene and toluene on a mixture of coal and silica gel a linear dependence of the adsorbed amount  $A$  of the benzene respectively the toluene vapor and the vapor concentration  $C$  (or  $C/A$  and  $C$ ) and at higher temperatures presenting the case of a kinetic equilibrium between condensation and evaporation, indicating the validity of Langmuir's concept on adsorption. By lowering the temperature the change obtained in the character of isotherms was attributed to a predominance of capillary condensation.

Russell and Ghering,<sup>66</sup> studying the sorption of oxygen by nickel catalysts, found that catalytically active nickel adsorbs rapidly up to 190° and that the adsorption of a considerable amount of oxygen is irreversible. The irreversible sorption increases with increasing temperature and with the activity of the nickel surface. A reversible adsorption of a large amount of oxygen takes place only at -190°. The velocity of slow sorption is small at this temperature, increasing with increased temperature and the activity of the catalyst.

Frost and Schapiro,<sup>30</sup> studying the dependence of the activity of catalysts on the pretreatment, concluded that catalytic activity is connected with lattice disturbances on the catalyst, especially with such places where the regular crystalline structure has been destroyed.

Ishimura,<sup>39</sup> studying the relationship between the area of the surface of acid earths and their catalytic activity, concluded that if catalysis does not occur simultaneously on the total surface but only follows on definite active centers, then the distribution of these centers on the surfaces of various kinds of earths is approximately the same. In other words, the value of catalytic activity depends on the surface content with uniformly distributed active centers, but not on the number of active centers of the same surface content. On the other hand, Ishimura considers catalytic activity and chemical composition as closely related and therefore the surface capacity is influenced by the chemical composition. The surface capacity is greater, the greater the ratio of  $\text{Al}_2\text{O}_3/\text{SiO}_2$  and the smaller the ratio of  $\text{CaO} + \text{K}_2\text{O}/\text{SiO}_2$ .

Munro and McCubbin,<sup>62</sup> studying the adsorption and catalysis in the

$\text{CS}_2 + \text{H}_2\text{O}$  reaction with alumina tubes as catalysts (air saturated with carbon disulfide is passed through tubes made of alumina with various content of water for a constant time with the same velocity at  $25^\circ$ ), obtained results indicating that adsorption precedes catalysis, but that there is no proportionality in general between the catalytic activity and the sorption capacity. The curves show distinctly that the maximum catalytic activity does not correspond to the maxima in the adsorption curves. Burstein and Kashtanov,<sup>16</sup> in a study of the relationship between activated adsorption and the paraortho conversion on charcoal at  $20^\circ$ , reached the conclusion that a change in catalytic activity as a result of activated adsorption can not be explained by a simple decrease in van der Waals' adsorption.

Although in many instances there is an apparent relationship between adsorption and catalytic activity, this does not indicate that strong adsorbing agents for reacting components of a catalytic system are good catalysts. Rideal<sup>63</sup> calls attention to Patrick's silica gel which, while possessing powerful adsorbing qualities and having a maximum surface area equal to 2,500,000 sq. cm. per gram, is catalytically inert for most reactions. A series of measurements on the adsorption of complex ammoniacal copper and silver ions on silica gel were made by Reyerson and Clark,<sup>62a</sup> who stated that the complex ions are so strongly adsorbed that they can not be set free again by treatment with 0.5*N* sulfuric acid. The adsorption depends wholly on the pH value of the solution and has at pH = 9.6 a maximum corresponding to about 10 millimol copper per gram of undialyzed gel.

An adsorption catalysis is one in which the chemical reaction occurs between molecules or atoms previously adsorbed on the surface of the catalyst, the adsorbed layer being considered the actual place where a reaction of this type takes place. In the case of a heterogeneous gas catalysis, the amount of gas active in the reaction is given through the amount of gas adsorbed. The amount of gas adsorbed is, in itself, a function of the adsorbent. Therefore, the characteristics of the adsorbent involved in catalysis is of great significance: (a) differentiating between the pure catalyst which is the adsorbent and the mixed or the impregnated catalyst on a carrier participating as an adsorbent; (b) determining the nature of the adsorbent in general, whether hydrophilic or hydrophobic, and (c) ascertaining whether the total surface of the adsorbent participates in a catalytic reaction, or whether there are certain centers, spots, or skins, the catalytic behavior of which is determined both qualitatively and quantitatively.

Considering the most elementary cases of adsorption catalysis in which the catalyst is the adsorbent, it must be remembered that in order to obtain a good adsorbent it is not alone sufficient to produce the greatest dispersion (porosity) corresponding to the maximum specific surface,  $S_0$ . In complete adsorption,  $A$  is the product of two factors, namely, specific surface  $S_0$  and specific adsorbability  $\Gamma$ ;  $A = \Gamma \cdot S_0$ . It is assumed that by "activation" through different methods of pretreatment, an increase in both factors may be attained. Heating charcoal up to  $850\text{--}1000^\circ$  in a

stream. of water vapor or carbon dioxide leads to an activation of the surface of capillary micropores and frees them from adsorbed substances and tarry compounds often remaining from the process of preparation.

Many successful methods for activating and purifying charcoal (adsorbent) have been proposed by a number of investigators.<sup>22, 24, 41</sup> The specific surface of activated charcoal has been calculated to be  $3 \times 10^6 - 10^7$  cm.<sup>2</sup>/g., and the diameter of the micropores, 3-9  $\mu$ m, the greatest factor in the formation of this unusually large surface. The specific surface,  $S_0$ , of a porous skeleton of silica gel obtained by slowly drying out  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  to maintain unchanged the porous structure and then heating at 700°C., was found to be about 400-500 cm.<sup>2</sup>/g. Guiselin<sup>35</sup> emphasized the importance of porosity and surface action and suggested preparing catalysts with pores of known size and shape. Any further differentiation between degrees of adsorption may be attributed to the nature of the adsorbent. While charcoal is hydrophobic, silica gel is hydrophilic;<sup>62</sup> while charcoal adsorbs surface active substances very readily from aqueous solutions and practically not at all from organic solvents (hydrocarbons),<sup>36</sup> silica gel<sup>42</sup> may be used with success only for the adsorption of more polar substances and of water vapor from non-aqueous solvents as, for example, adsorption of vapors of organic substances from the air.

The relationship between the adsorption process and the catalytic reaction velocity was investigated by Taylor and Burns<sup>78</sup> in hydrogenating with metallic catalysts in which appreciable adsorption of reacting gases was noted. Pease,<sup>57, 58</sup> hydrogenating ethylene with copper, stated that the activity was due to high temperature rather than to the influence of the adsorption ability. It is apparent that in some cases high adsorbability is accompanied by high catalytic activity and in others to the contrary, although in the first instance no definite ratio has been established between the two factors.

It is known that small amounts of poisons, such as carbon monoxide for example, in catalytic processes are not sufficient to saturate the entire surface of the adsorbent, yet are able to reduce its activity to zero, as well as alter the relationship of the adsorption capacity of the two gases, using one and the same catalyst prepared by different methods. This is the basis for Taylor's assumption which postulates that the catalyst surface is not homogeneous and the catalytic activity of surfaces not uniform.

Russell and Taylor<sup>67</sup> sought proof for this assumption in the promoter action, ascribing its activity to an improvement in the surface, not to an increase in the surface, and found that on hydrogenating carbon dioxide to methane over nickel catalyst with thorium oxide as promoter the reaction was accelerated ten times, although the adsorption capacity increased at the same time only up to 20 per cent. It is likely that that part of the surface active in the catalytic reaction is specific for each reaction. Taylor suggested that in oxides the metal ions of the crystalline lattice serve as catalysts for hydrogenation and dehydrogenation, while the oxide ions are centers of activity for hydration and dehydration reactions. Rideal<sup>163</sup> emphasized the fact that the effective surface in ordinary catalytic substances is even less than that calculated from Patrick's data, if

$2.5 \times 10^6$  cm.<sup>2</sup>/g. is the effective area of his silica gel. If  $3 \times 10^8$  cm. is the average molecular diameter, then the effective molecular surface area should be  $2.5 \times 10^{21}$  molecules per gram, or 240 grams would be sufficient to adsorb a gram molecule of reactants. ( $N = 6.06 \times 10^{23}$ ). In certain reactions, every atom of the surface may be active; in others, only a fraction, and this may be considered as an explanation for the difference in the sensitiveness to poisons.<sup>83</sup>

Natanson<sup>53</sup> attempted to differentiate the activated iron nitride from the non-activated one. He found that the micro-crystals of both nitrides have practically the same size. By calculating the total number of surface atoms of nitrogen for each gram of the nitride,  $4.66 \times 10^{-4}$  gram atoms of nitrogen were determined for the activated and  $9.02 \times 10^{-5}$  gram atoms for the non-activated. For the total number of nitrogen atoms on the surface of all micro-crystals of the activated nitride the value of  $30.58 \times 10^{19}$  atoms or  $5.05 \times 10^{-4}$  gram atoms per gram are obtained. Comparing the latter with the above value  $4.66 \times 10^{-4}$ , Natanson concludes that almost the total surface of the micro-crystallites serves as a boundary between the gas-phase and the solid body. Since the non-activated nitride possesses a surface five times smaller than the activated nitride, their micro-crystallites being almost equal in size, the activator ( $\text{Al}_2\text{O}_3$ ) in the case of activated nitride prevents tight uniting of the crystallites, the crystals in the activated nitride being arranged loosely so that practically all its surface lies free, while in the non-activated nitride as a result of a tight packing the contact or the linking surface of crystallites is considerably greater and therefore the free surface is smaller.

Rayleigh and Hardy, also Langmuir,<sup>45</sup> indicated the probability of limiting the seat of catalytic activity to a film of reacting substances adsorbed on the surface of the catalyst. Foresti<sup>29</sup> entertained the belief that a surface of a catalyst, nickel for instance, is composed of adsorption centers varying in their ability to adsorb, and that the catalytic activity is determined by centers able to adsorb the gas retained by the strongest bonds.

Taylor<sup>74, 75, 79</sup> attempted to explain active centers or "extra lattice atoms" by studying conditions governing their catalytic activity with respect to metals, crystalline catalysts and boundary surfaces. Atoms composing a metal surface are present in varying degrees of saturation. Unsaturation is assumed to vary from atoms completely saturated by neighboring atoms to those in which surface atoms are attached by a single valence to the remainder of the surface and are but one step removed from the condition of atoms in a gaseous state. The varying degrees of saturation correspond to varying degrees of catalytic activity. In a crystalline surface atoms are distinguished by their degree of saturation according to the position they occupy in the crystal lattice, whether: (a) in the plane; (b) in the angles, or (c) in the corners. Taylor attributed the greatest catalytic activity to the most unsaturated atoms, and the least catalytic activity to the most saturated atoms in the plane of the crystal surface. Pease and Taylor<sup>59</sup> found a higher catalytic activity at

the boundary surface of Cu/CuO as compared with the main surface of the two phases.

The "active centers" theory of adsorption catalysis has been modified by a number of investigators principally with reference to the position in the catalyst identified as one of high catalytic activity. Schwab and Pietsch<sup>71</sup> consider edges and corners of crystals as the "active spots" of a catalyst which shifts Talyor's boundary surface conception to that of irregular boundary lines separating two phases. The localization of the catalytic action at linear discontinuities appears to Schwab and Pietsch as reasonable due to the fact that crystal edges and their boundary lines may display an increase in the velocity of germ formation and reaction ability and therefore in catalytic activity because of an increased field of action. These investigators supported this viewpoint by a number of examples cited in the literature; Smekal assumed that the increased activity with decreasing size of crystals was a criterion for the greater activity of crystal edges or imperfect crystals compared to smooth surfaces; or that when the size of a crystal decreases the ratio of the crystal edges to the surface increases.

Volmer<sup>84, 86, 87, 88</sup> and his co-workers considered two dimensional phase boundaries not from Langmuir's or Taylor's viewpoint of "fixed" adsorbed molecules, but from the viewpoint of crystal growth. According to Volmer,<sup>86</sup> molecules in the adsorbed layer move about on the surface in two dimensions similar to gas molecules which move in three dimensions. It has been proved that the two-dimensional mobility of the adsorbate and its series of reactions proceed at phase boundary lines. Cassel,<sup>16</sup> as well as Schwab and Pietsch,<sup>70, 71</sup> conceived the idea that the place of active atoms and therefore of catalytic activity were homogeneous, one-dimensional discontinuities of the surface. As the three-dimensional gas streams toward the total surface of the catalyst, so the two-dimensional gas streams toward the active lines and reacts there. The idea that "active centers" were in themselves uniform homogeneous formations was expressed by Constable.<sup>18</sup> He also pointed out that among centers with off-grade energy, only the most active centers were kinetically decisive as a result of their excessive reaction velocity.

Smekal<sup>73</sup> and Zwicky<sup>92</sup> went even further, for they considered every irregularity in crystal growth appearing on the surface as an "active spot" of greater attraction power and therefore of greater catalytic activity. The imperfections occurring in all crystals are increased by admixtures of foreign substances or by increasing the rate of crystal growth. The more rapidly a substance is crystallized the greater the probability for the occurrence of such imperfections. The high temperature at which crystal growth takes place induces the same kind of imperfections or favors an increase in the number of "active spots." Smekal estimated that the number of active spots varies between  $10^{-3}$  and  $10^{-5}$  of crystal units, depending upon the conditions for crystal growth. In Sei's<sup>72</sup> interpretation the number of "adsorption centers" is much less than the number of molecules forming the crystal surface, and each adsorption center is able

to bind only one molecule (adsorption of molecules in a gaseous state on a solid).

Balandin,<sup>6</sup> in his multiplet theory of adsorption catalysis, refers to a "checker-board" surface the nature of which is determined by the chemical composition of the substances composing the surface. If the points of adsorption are close to each other, then different parts of one and the same molecule may be adsorbed by more than one point of the surface causing a stretching or even a tearing apart of the molecule. If the molecule is very strongly adsorbed at only one point, then the adsorption will be strong, but practically without activation. Balandin illustrated his hypothesis by the dehydrogenation of alcohol. If OH and H in the alcohol are adsorbed by one spot and the molecule of alcohol torn apart, then the H and O on that spot will unite to form water and the remainder of the molecule will form ethylene. If, on the other hand, one active spot adsorbs two hydrogen atoms and the other types of spots the remainder of the alcohol molecule, then the dehydrogenation will proceed to the formation of aldehyde. Therefore, the specificity in the action of catalysts may be attributed to the presence of "active spots" having the ability of attracting different atoms of the same molecule. Balandin believes that his hypothesis may also account for the poisoning effect occurring in catalysis due to traces of foreign substances without effecting greatly the adsorption capacity in general because of a retardation in adsorption on any one of the different kinds of points located on the surface.

Born and Frank<sup>13</sup> considered the principal factor in adsorption catalysis the maintenance of a continued association of the reaction components over a long period of time due to adsorption. In the gaseous state the quantum mechanical effect of the passage through an energy threshold does not occur because the time interval involved in the collision of gas molecules is too short (about  $10^{-13}$  sec.); even if the density of a gas were high, effecting numerous collisions, there is little or no possibility for marked conversions to occur. After adsorption takes place, both reaction components form a kind of "monomolecular skin," especially well developed on "active centers," and it is assumed that this skin is maintained for a period of time expressed in seconds.

While Taylor thought that his "active centers" possess the ability to fix by adsorption gas from the gas phase separating thereby large amounts of adsorption heat and decreasing the strong binding producing thereby conditions necessary for a successful catalysis, Garner and Kingman<sup>33</sup> and Garner, McKie and Knight<sup>32</sup> assume that first the loosely adsorbed molecules align themselves in the surface before they are bound to the most active places with a measurable heat of adsorption.

Audibert<sup>5</sup> opposes the hypothesis of "active centers" by assuming that adsorption anomalies are based on local irregularities in the crystal structure of the adsorbent indicated by abnormal values of evaporation heats of adsorbent atoms due to local distortion of the crystal lattice. The existence of mixed crystals and unstable forms of solid bodies recognized by abnormally small densities and indistinct x-ray diagrams was considered by Audibert as proof for such a change in the elementary unit of the crystal.

Harker,<sup>37</sup> studying hydrogenation of ethylene over copper on diatomaceous earth, considers that both adsorbed hydrogen and active copper centers are responsible for catalysis. He postulates that activated hydrogen molecules attach themselves to the active copper centers forming complexes which are readily decomposed by ethylene forming ethane. A certain mobility is necessary in order that activated hydrogen molecules may be attached to the active copper centers. Adsorption of ethylene or ethane reduces the activity of the catalyst by impeding the movement across the surface causing a decrease in the rate of the reaction.

A study of the literature on catalysis indicates that the application of catalysts in a pure or mixed form or impregnated on a carrier is specific with respect to the type of catalytic reactions. There are certain reactions which proceed better with pure catalysts while others, on the contrary, favor mixed catalysts, and those impregnated on a carrier. The function of mixed catalysts or those impregnated on a carrier in adsorption catalysis is to improve the activity of the catalytic process, and it is recognized that this kind of activation may imply: (a) an increase in the adsorption surface by changing the degree of dispersion and at the same time the number of unsaturated atoms; (b) the formation of a more favorable contact; (c) the protection of the catalyst from sintering processes, and (d) providing new points of attachment for the molecule differing from those of the original substance, or providing better spacing of the active points. These factors are basic also for the recognized influence of the pretreatment of the catalyst on its activity.

The mechanism by which activation, or improvement of the activity of a catalyst by mixing it with other catalysts or incorporating it with another substance on a carrier, operates has been a problem for many investigators. There has been a general tendency on the part of mixed catalysts, as well as catalysts on carriers, to partake of the relationship existing between the structure of the catalyst surface and the catalytic activity under these conditions.

Long, Frazer and Ott<sup>47</sup> investigated the influence of the lattice constant and lattice type upon the catalytic activity of mixed metal catalysts, such as nickel-iron, nickel-cobalt, nickel-copper and iron-cobalt, prepared under similar conditions of precipitation from hydroxides, dehydration and reduction. The structure of mixed catalysts was followed by making x-ray diagrams of their powders and their activity determined by hydrogenation of benzene to cyclohexane. The lattice constant and the lattice type of mixed crystals was found to depend on the composition of the mixture and the nature of the components. In this hydrogenation reaction, using either pure metals or mixed catalysts, those with plane-centered lattices are catalytically active, while those having space-centered lattices are catalytically inactive. They also assume that activity depends on the magnitude of the lattice constants.

Frost, Jvannikow, Shapiro and Zolotow<sup>31</sup> endeavored to establish a relationship between the structures of copper and zinc catalysts used in the decomposition of methanol. The x-ray diagrams showed that while



the lattice dimensions of zinc oxide for all observed catalysts remained unchanged contrary to the results of Aborn and Davidson,<sup>C. 1930, 1 3639</sup> a broadening of the copper lattice is obtained with an increase in the amount of zinc oxide in the mixture, which is also a function of the reduction and application of the catalyst. In general, this investigation indicates that an increase in the catalytic activity of mixed catalysts can not be attributed to changes in the lattice dimensions, but rather to places in the catalyst in which the regularity of the crystal lattice is disturbed. Such disturbances or deformations in the crystal lattice may readily occur in mixed catalysts and may be stabilized as well. Depending upon the ingredients added, these disturbances or deformations vary in nature for one and the same catalyst.

This problem was further investigated by Wagner, Schwab and Staeger<sup>89</sup> who examined Debye-Scherrer diagrams obtained for various binary mixed catalysts as well as their components and found that in those cases in which a "structural" or "synergetic" strengthening could be assumed from the kinetics of the reaction, the mixture showed an unchanged lattice for both components, while in those cases in which the kinetics revealed a poisoning effect or anomalous strengthening, the x-ray diagram proved the presence of chemical compounds. In the case of copper-nickel mixed catalysts for hydrogenation purposes, the question whether the catalytic activity itself is based on the enlargement of the lattice or is dependent on the co-existence of many types of decidedly enlarged lattices of mixed crystals is still open for discussion. The statement that an increase in the activity of mixed catalysts is due in some cases to the origin of mixed crystals has been emphasized and experimentally verified. While classic chemistry draws a sharp demarcation between mixed crystals regulated by the law of multiple proportions and compounds, the modern chemistry of metals<sup>19</sup> considers that the mixed phase for every metal originates in the action of an affinity not bound to stoichiometric concentrations, but acting within the interval of total concentration. Therefore, the new conception assumes that each phase has its affinity, and its character as a compound and is estimated from the magnitude of that affinity in the mixed phase.

There are definite rules governing the origin of this affinity, as well as the influence it has upon the lattice form, namely, (a) van der Waals' forces of attraction; (b) the Hume-Rothery relation of the electronic number, and (c) the mutual attraction of the unsaturated atomic shred. Depending upon the existence of these three types of affinity, three groups of mixed metallic crystals are differentiated: (a) mixed group; (b) Hume-Rothery alloy group, and (c) Zintl alloy group.

In the Zintl group the affinity is due principally to van der Waals' attraction forces and to electrons bound rigidly to single atoms. This group is composed of alloys of noble metals and their components show very little change in type of lattice. The affinity in the Hume-Rothery group has its origin in valence electrons which are apparently free in the so-called "electronic gas," assuming that there is no complete number of electrons per atom in this "gas." In this group are classed alloys of silver,

copper, gold, iron and platinum with magnesium, cadmium, zinc, tin and others, having a decided change in type of lattice in the intermediate phase. For the mixed group the affinity is assumed to be due to the action of atomic shreds remaining when one valence electron has been broken off. Although this group has free electrons, it has no Hume-Rothery phase, and this is explained by the fact that in these alloys every atom possesses the same valence electron number. To this group belong alloys of silver, copper and gold, as well as iron and platinum mixed with one another; they have intermediate phases with a slight change in lattice type at low temperature but at high temperature, only mixed crystals are present.

Levy and Haardt<sup>46</sup> and Taylor, Kistakowsky and Perry<sup>80</sup> found that samples of pure catalysts with small particle sizes possess better catalytic activity:

Catalyst	Size ( $\mu$ )
Platinum.	4.8 -11.27
Palladium.	4.98-11.10
Rhodium.	2.20
Iridium.	1.16
Ruthenium.	1.92- 3.61
Osmium.	1.70- 2.70

Apparently a relationship exists between an increase in the catalytic activity of mixed catalysts and the degree of dispersion of the catalyst. On the other hand, Frost, Jvannikow, Shapiro and Zolotow<sup>31</sup> are of a contrary opinion, stating that in the effect of the degree of dispersion they found the adsorption ability to reverse in proportion to the average size of a crystal, while the catalytic ability decreases rapidly with an increase in temperature. They also determined the greatest increase in catalytic activity of zinc-chromium catalysts when the tempering temperature was about 100°, or slightly below the temperature at which a rapid formation of mixed crystals (spinel) occurs.

Eckell<sup>25</sup> analyzed the relationship between the catalyst structure and the chemical conversion of aluminum oxide in the ferric oxide lattice by determining the particle sizes from x-ray diagrams, as well as from electron reflection diagrams. The latter method recognizes particle sizes between 100 and 10Å, whereas the x-ray method proves the particle sizes to be between 3.0 and  $1.0 \times 10^{-6}$  cm. Pure ferric oxide was the coarsest preparation, while a mixture of 89.92 per cent ferric oxide and 12.68 per cent aluminum oxide was found to be the finest. The electron reflection diagrams seem to indicate a parallelism between velocity constant and dispersion, but as derived from Arrhenius' equation no relationship was found between dispersion and activity. The higher activity of the mixed catalyst has been assumed to be due either to a decided increase in the total surface, or to a change in the course of the reaction through intermediate reactions as a result of a decrease in the activation heat. The relation between  $K_0$  and  $Q$  of Arrhenius' equation indicates that both are functions of the energetic state of the surface.

From experimental evidence it is apparent that finely divided metals used as catalysts display higher activity when produced by reduction at

low temperatures. The metals obtained by reduction at low temperatures have a high specific surface which may be considerably reduced by melting together particles at high temperatures, the so-called "sintering" effect. As a rule, surface catalysts are substances of very high melting points with an optimum temperature for use in adsorption catalysis which must be always considerably below this melting point. Silver, copper, iron, platinum and palladium deposited electrolytically as a fine dispersion show the phenomenon of sintering at temperatures considerably lower than their ordinary melting points.<sup>90</sup> The melting point is altered not only by the fine subdivision, but by vapor pressure and solubility as well. The sintering effect is thought to be due to an abnormal vapor pressure and to the solubility of the finely dispersed substance. In addition to the temperature factor, aging of the catalyst plays an important role in the sintering effect.

Dobytschin and Frost<sup>20</sup> observed aging processes of thin palladium layers used as catalysts and found that they were accompanied by a sintering process. X-ray diagrams revealed that fatigued layers had crystal sizes 250-1000Å, while the crystal sizes for fresh layers of metal were found to be less than 40Å. The growth of crystals in fatigued layers influences only slightly the limiting values of hydrogen adsorption, while it decreases readily the sorption and desorption velocity. The sorption velocity on fresh layers is considerable and independent of pressure. The sorption velocity on sintered layers is strongly influenced by pressure. The sintering process or crystal growth accompanied by a decrease in catalytic activity is not evidence of desorption during sintering, as stated by Bastow<sup>10</sup> and Müller and Schwabe.<sup>51</sup> Dobytschin and Frost's experiments with palladium plus hydrogen and platinum plus nitrogen showed that while desorption occurred in less than 2 minutes, sintering took place only when the layer lost more than 95 per cent of the previously sorbed hydrogen. They also found that hydrogen, as well as other gases, have a tendency to slow down considerably the sintering effect.

Natta,<sup>54</sup> studying the structure of catalysts when taken singly and when mixed with chromic oxide or aluminum oxide, considered these as reducing the rate of growth of zinc oxide granules by retarding the natural decrease in the surface of the catalyst, that is, sintering effect (at 400-500°C.). Since these oxides do not penetrate into the solid solution in the zinc oxide lattice as is the case with copper, cobalt, manganese, iron, magnesium and nickel oxide, they do not increase the activity of the surface atoms of the catalyst by distorting the lattice. Natta explains the increase in catalytic efficiency on mixing of the two oxides by an increase in the internal area of the oxide and its adsorptive capacity and not due to any change in surface energy of the atoms. If this interpretation is applicable, then no great difference should exist between heats of adsorption for hydrogen and carbon monoxide on zinc oxide, or chromic oxide taken singly and that of the mixed catalyst.

Russell and Ghering,<sup>66</sup> studying the sorption of oxygen by nickel catalysts, found that sintered and regenerated nickel surfaces possess certain similar but also some declining sorption properties.

Fajans<sup>28</sup> is of the opinion that to each sintering temperature corresponds a state of definite surface activity or definite configuration. When investigating sintering of nickel catalyst in the *para*-hydrogen conversion, Fajans found that the activity is higher when sintering starts at lower temperatures. After 10 minutes sintering the catalyst acquires an activity which does not change after many hours of heating. If the temperature is of the order at which sintering occurs, then the end value reached is almost independent whether the starting catalyst was prepared by reduction at low temperatures (high activity) or at high temperatures (low activity).

Another important factor in the activity of a catalyst is the relative position and the distances of active atoms—the so-called “steric factor.” In case the substance admixed with the catalyst is not in itself a catalyst but an inert substance, its function is that of a carrier which, in addition to preventing recrystallization (transition of small crystals into large and less active crystals), increases the active surface of the catalyst, as well as its stability; in other words, increasing the time of its effectiveness by separation of individual catalyst particles. In case the catalyst is an adsorbent, it is assumed that adsorption takes place by distribution between the active metal centers and those of the carrier expressed by a blockade of active centers.<sup>69</sup> It is further recognized<sup>40</sup> that in order to accelerate a reaction, a “coactivation” of active centers is to be anticipated. Coactivation of active centers by heat of reaction indicates that a catalyst on a carrier contains centers of varying activity, that is, a reaction in force activates the center of maximum activity *A*; the reaction heat from *A* activates neighbor center *B*, while the reaction heat from neighbor center *B* activates not only neighbor center *C*, but also *A*. When an equilibrium is reached between heat gained and heat lost, the reaction proceeds with a constant velocity. The coactivation factor is limited for the amount of inert material used as a carrier. The distance between neighbor centers must not be too great so that the distance between active centers will not be greater than in the case of a pure catalyst.

Homogeneous distribution of the catalyst in the mass of the carrier is also important. With palladium catalyst well distributed on kieselguhr, Joshikawa succeeded in hydrogenating acetylene to 90 per cent ethylene by using equal amounts of acetylene and hydrogen. Köppen<sup>43</sup> believes that kinetics is an explanation for the dependence of the activity upon the distribution of a catalyst on a carrier which may be expressed according to the time interval necessary for the conversion and is a function of the size of single platinum crystallites. It has also been claimed that oxides can be used to advantage as carriers because they are poor heat conductors and favor the accumulation of heats of reaction.

Adadurow<sup>1</sup> is not in agreement with Köppen's mechanical adsorption theory on the influence of a carrier in hydrogenation and dehydrogenation processes with platinum catalyst, for he emphasizes the influence of the carrier field on the catalyst field. In investigating the influence of form and size of the contact mass (tin oxide-barium) on the oxidation catalysis of sulfur dioxide, Adadurow and Gernet<sup>3</sup> concluded that for every form

and size of the contact mass an optimum volume-velocity ratio, gas concentration and contact duration are characteristic. The higher the volume-velocity ratio the higher the contacting value of contact fragments, the magnitude of which, in comparison to the effective surface and to the free space unit, appears to be very small. In the case of contact fragments having a greater surface, such an influence is not apparent, for it may be due to an increase in the number of active centers available in the equilibrium state. With regard to the shape of a catalyst, consideration should be given to the greatest specific geometric surface which it can attain, for this offers the least resistance to the gas stream and the greatest effective surface to free space unit. On the other hand, the greater the uncovered surface the greater the influence of contact duration upon the conversion yields at low temperatures which, together with an increase in temperature resulting in the origin of a greater number of active centers upon the surface unit, become equivalent.

Adadurow<sup>2</sup> pointed out that the carrier may either (a) improve the catalytic activity of the catalyst as in hydrogenation processes using platinum on silica gel or charcoal, or (b) make it worse, for example, when palladium is used as a hydrogenating catalyst on barium sulfate or pumice. The introduction of a catalyst on a carrier may be followed by a complete stop of catalysis or, under other circumstances, it may change completely the direction of the reaction. Thus, for example, the specific aldehyde catalyst, zinc oxide, may be converted into a specific ethylene catalyst by placing zinc oxide on charcoal. The carrier may change the sorption properties of the catalyst by making it more or less sensitive to catalyst poisons.

Charmadarjan and Brodowitsch,<sup>17</sup> investigating the influence of the carrier upon the catalytic properties of vanadium pentoxide in the oxidation of sulfur dioxide by air, considered manganese dioxide to act best among such carriers as asbestos, infusorial earth, glass, porcelain and quartz, and noted that the action of activators, such as copper sulfate, ferric sulfate, barium chloride and manganese sulfate, is a function of the nature of the carrier. They emphasized also that the method of covering and the thickness of the layer greatly influence the effectiveness of the catalyst. Vanadium pentoxide precipitated from a colloidal solution by hydrochloric acid gave greater catalytic activity than when prepared by heat coagulation. A strong dependence of activity on the concentration of the solution was shown for ammonium-*m*-vanadate catalyst heated to 440° to attain a uniform spreading.

Adadurow<sup>2</sup> attempted to estimate the actual part a carrier plays in catalytic processes. He considers the carrier not as an indifferent foundation for the catalyst, but attributes to it a function of a deformer and polarizer of atoms as well as molecules of the catalyst, changing thereby the properties of the latter. The deformation action is assumed to be the greater the smaller the atomic radius and the higher the valence of the carrier. On the other hand, the deformability of the catalyst is greater, the greater its atomic radius and the smaller its charge. The greater the

deformation action of the carrier, the greater the change effected in the activation energy.

Baly<sup>8</sup> found that kieselguhr adsorbs certain hydrous metallic oxides, such as those of aluminum and nickel, rendering a very stable system. He considered the great advantage of a supported catalyst to lie in the fact that a reaction will be promoted at a lower temperature, which is of importance, especially in the case of a reaction product which is unstable at a high temperature. By the use of a suitably supported catalyst a reaction may be realized which would be impossible with a simple catalyst due to the instability of the reactants and resultants at high temperature.

A given surface possesses some specificity in that it will act as a catalyst for some reactions and not for others. In the case of supported catalysts evidence was obtained that an optimum condition exists for the adsorption of alumina and other substances by kieselguhr. In case of alumina, the optimum condition is obtained when kieselguhr is completely coated by a unimolecular layer. In case of nickel monoxide or cobaltous oxide, the optimum condition corresponds to kieselguhr being completely coated by a termolecular layer (a layer of elementary unit cells of these oxides). Baly assumes the existence of a stoichiometric relation between the quantities of two substances adsorbed by two equal areas of kieselguhr surface. In the case of alumina and water, both of which are adsorbed in unimolecular layers, the number of molecules adsorbed by two equal areas is in the ratio of two aluminum hydroxides to three of water.

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## THE ROLE OF DIFFUSION IN CONTACT CATALYSIS

Adsorption processes in the simpler cases may be due to a condensation or agglomeration at the surface of the adsorbent; other possibilities, such as penetration into the solid must be taken into consideration in many cases of contact catalysis. It is evident that occlusion or diffusion may accompany adsorption in catalytic processes. Adsorption and diffusion are bound together very definitely in the case of the adsorption of gases by solid metals. Metals have a high adsorbability for gases. As shown in Table 1, there is a definite temperature at which adsorption takes place for a particular gas, as well as for a particular metal.

Table 1. Adsorption of Gases by Metals at Constant Temperature.

Gas	Metal	Temperature (°K.)	Gas	Metal	Temperature (°K.)
H <sub>2</sub>	Ni	83	N <sub>2</sub>	W	293
H <sub>2</sub>	Pt	195			
H <sub>2</sub>	Fe	90-195	N <sub>2</sub>	Ni	98-173
H <sub>2</sub>	ZnO	273	CO	Cu	273
N <sub>2</sub>	Fe	273	CO	Fe	195

Some metals which adsorb very large amounts of gas do not even change in appearance. How high the adsorption capacity may be and how it varies in single cases is illustrated in the following table:

Table 2. Volume Adsorption of Gases by Metals.

Metal	Volume H <sub>2</sub> Adsorbed
Pd sponge.	680-850
Pd (previously glowed).	940
Pd black.	875
Pd hydrosol.	926-952
Pd (alloyed with less than 70% Ag).	At least as much as the pure Pd
Co (reduced).	153 (Moissan)
Au (finely dispersed).	46
Fe or Ni (reduced).	19
Cu (reduced).	4
	Volume O <sub>2</sub> Adsorbed
Pt black.	100

It is believed that a parallel exists between the ability of gases to be adsorbed by metals and the diffusion of gases through them and that the two phenomena are related through some common property. The amount of hydrogen penetrating on diffusion is not proportional to the pressure because part of the hydrogen molecule is dissociated, but the amount of diffused hydrogen is proportional to the density of dissociated molecules. According to Langmuir's data (Table 3), the number of molecules dissociated varies with the temperature.

Table 3.

Temperature (°C.)	Number of Molecules Dissociated (out of 10,000 molecules)
2000	33
2300	140
2500	310
3100	1,700
3500	3,400 etc.

On the other hand, a palladium plate measuring 1.1 mm. in thickness permits passage through a surface 1 mm.<sup>2</sup> of 423 ml. and 2,400 ml. hydrogen at 240° and 1000°, respectively, in one minute. Thus, hydrogen entering the metal surface spreads among its atoms being converted thereby into the atomic state. For the solubility of hydrogen in metals, it has been found that  $m = K \sqrt{P}$ , *i.e.*, the solubility is proportional to  $\sqrt{H_2}$ , and therefore also to the square root of the density of the hydrogen. This confirms the fact that hydrogen is actually dissolved in the metal in the atomic state. Lewis<sup>20</sup> assumed that for the dissociation of hydrogen, a short wave radiation energy coming from the metal in which hydrogen dissolves, is necessary. The existence of this radiation is a function of



temperature; at ordinary temperature the radiation is small, but at high temperatures it is essential and depends on the heat of melting of the metals, the latent heat of melting being the source of energy which leads to the dissociation of hydrogen in metals. Therefore metals dissociating hydrogen must have higher values of latent heat of melting. The dissolution of hydrogen in melted metals is much higher than in solid metals; as a matter of fact, for copper it is three times as much; for nickel and iron, two times.

Table 4.  
(Honda<sup>16a</sup>)

Metal	Latent Heat of Melting per gram atom	Metal	Latent Heat of Melting per gram atom
Platinum.	5360	Silver.	2270
Palladium.	3860	Aluminum.	2160
Iron.	3348	Zinc.	1840
Nickel.	2710	Sodium.	730
Copper.	2650	Mercury.	562

St. Claire, Deville and von Graham<sup>32</sup> proved that hydrogen penetrates heated iron, palladium, and platinum. Troost<sup>38</sup> recognized diffusion of oxygen into silver heated above 770°. Aluminum and silver were found to be impervious to hydrogen, while copper was inaccessible to carbon monoxide and sulfur dioxide.

Lichtenberg<sup>21a</sup> studied the diffusion of hydrogen *in statu nascendi* through aluminum using the Ploum and Bardenheuer arrangement, but observed no diffusion of atomic hydrogen. The same result was found with a more sensitive arrangement permitting the measuring of 0.05 atmosphere pressure changes. It is concluded therefrom that hydrogen does not diffuse through aluminum *in statu nascendi*. Nickel and iron were impenetrable to carbon monoxide even at 1000°. The diffusion of a gas into a metal occurs at a rather high temperature, platinum<sup>28</sup> proving to be an exception, because it permits diffusion of hydrogen at comparatively low temperature, although in small amounts. The diffusion velocity increases with increasing temperature. In the case of palladium and nickel, hydrogen penetrates at high temperatures with a velocity equal to that in a vacuum reaching a state of equilibrium almost immediately. Pease<sup>24</sup> proved that adsorption of carbon monoxide on copper occurs up to a definite amount, but is considerably increased by added pressure.

The diffusion of gases into a metal has been related to the solubility of the gas in the metal. It has been recognized that absence of diffusion ability and insolubility go hand in hand, while soluble gases, not necessarily but very often, have a diffusion ability. This led to the origin of two terms: "diffusion" and "occlusion." Many diatomic molecules dissolve in metals in the atomic form,<sup>34a</sup> and the rate of solution is found to increase with the square root of the pressure. In Fe, Co, Ni and Cu, hydrogen dissolves as protons; in Zr and Ti, hydrates are formed. Equations for the solubilities have been developed by Fowler and Smithells<sup>8a</sup> and the rates of solution have been studied by Dunn and Ward,<sup>6a</sup> Melville,<sup>23a</sup> and Smithells and Ransley.<sup>36a</sup> The processes of diffusion of the

hydrogen or oxygen atoms, whether extra or intra lattice appeared to be of the activated type. According to Pilting and Bedworth, when oxygen penetrates a film of cuprous oxide to the underlying copper, the rate of oxidation becomes constant above a certain critical oxygen pressure. The critical pressure is very high when the cuprous oxide consists of very small crystals, and very low for macro-crystals.

McBain,<sup>23</sup> studying the adsorption of iodine by charcoal, produced evidence that the phenomenon of adsorption is frequently accompanied by an "intra solid diffusion" process resulting often in the formation of solid solutions or compounds within the solid material. While surface adsorption is rather an instantaneous reaction, "intra solid diffusion" is an extremely slow process.

von Graham was the first to prove that hydrogen occluded by palladium is especially reactive, while Ramsay<sup>25</sup> found that hydrogen diffusing through palladium reduces nitric oxide and nitrogen dioxide at temperatures at which these gases are inactive. Sieverts<sup>35</sup> assumed that the special reactivity of hydrogen *in statu nascendi* had its analogy in the increased activity of the occluded or diffused gas. Hoitsema<sup>16</sup> and Winkelmann<sup>41</sup> interpreted the increase in activity as due to the splitting into atoms of molecular hydrogen in diffusion and occlusion processes. Sabatier and Senderens<sup>31</sup> ascribed the ability of nickel to accelerate the reaction between hydrogen and unsaturated hydrocarbons to its high dissolution of hydrogen and assumed the formation of "hydrides" as intermediate products. Sieverts<sup>35</sup> opposed this viewpoint by stating that the word "hydride" as a chemical compound of the order formed by alkali metals with hydrogen is inconsistent in the present case and that there is a greater probability of hydrogen being converted by occlusion into a specially active state.

Many difficulties are encountered in the recognition of heavy metal-hydrogen compounds. Hammerwald<sup>15</sup> is of the opinion that there exists a chemically bound hydrogen because of the fine structure of the adsorption edges revealed by x-ray. Coehn's<sup>8</sup> experiments indicate that the hydrogen penetrating a metal is in the dissolved state and will move under the influence of an electric current and therefore assumes the presence of free protons in the metal. Rupp<sup>30</sup> thought that hydrogen penetrated deeply into the metal lattice, but questioned whether this hydrogen would function in a catalytic reaction. Schmidt<sup>33a</sup> implies hydrogen solution in metals, involving ion formation in the case of hydrogenations.

Leipunski,<sup>19</sup> emphasizing the fact that kinetics of activated adsorption is characterized by the presence of a "steric" factor, ascribes its existence to a diffusion process either on the surface or on the inside of the lattice.

Sen<sup>34</sup> draws a parallel between the diffusion process of elements in a solid state and the process of amalgam formation, the difference being that the diffusion process proceeds slowly and without breaking up of the metal lattice. It is also emphasized that the element with the smaller atomic diameter penetrates into the other. The relation between the smallest atomic diameter in the lattice and the diffusion direction has been confirmed for Cu-Pt, Cu-Zn, Fe-Ag, Au-Pb and Fe-C.

Confusion regarding the role of diffusion in adsorption catalysis is

often found in the literature. Lewis<sup>20</sup> emphasized the fact that data on the catalytic oxidation of sulfur dioxide obtained by Bodenstein and Fink<sup>4</sup> may explain the mechanism of adsorption catalysis by taking into account diffusion, as well as adsorption through a single layer. Fink's<sup>8</sup> equation, implying diffusion through a film of variable thickness for a given concentration of sulfur trioxide, is expressed thus:  $K = 1 / \frac{b}{p^1} + \frac{c}{p^2}$ .

The surface of the adsorbent quartz was found to be covered with an adsorbed film of carbon monoxide having a thickness proportional to the pressure of the gas. The reason for the reaction being directly proportional to the oxygen pressure and inversely proportional to that of carbon monoxide may be attributed to the fact that oxygen diffuses through the layer of carbon monoxide and comes in contact with platinum before it reacts with the carbon monoxide. On the other hand, the work of Bredig on the decomposition of hydrogen peroxide, as well as that of Greenwood and Taylor on the use of various carriers for catalytic agents, supports the fact that the catalytic activity is proportional to the area of the catalytic material used, and that intra-diffusion of the reactants into the interior of the solid plays only a minor role in catalytic phenomena.

Rideal,<sup>29</sup> in a further investigation of this problem, foresaw the necessity of determining the relationship between the mean diameter of a capillary fissure and the depth to which the catalytically active surface descends. It is a fact that in a gas mixture containing carbon monoxide, hydrogen and oxygen, subjected to surface combustion, the ratios of carbon monoxide to hydrogen vary, depending on the nature of the catalytic material. From this Rideal assumed that the viewpoint on diffusion was inconsistent for the reason that hydrogen has a greater mobility and should penetrate very rapidly into the adsorbed layer of carbon dioxide and water vapor surrounding the catalytic material and not into carbon monoxide which would burn more readily than hydrogen at low temperature, as was found to be the case.

It is generally assumed that diffusion takes place through molecules in the adsorbed layer, reaching the spots of activity on the surface. In other words, diffusion proceeds perpendicularly from the gas phase through an adsorbed layer of appreciable thickness. If diffusion rather than adsorption of gases takes place, a smaller coefficient of the reaction temperature would be involved. Bodenstein<sup>3</sup> actually determined temperature coefficients higher than those ordinarily anticipated from the diffusion of gases. The difficulty of clarifying the mechanism of adsorption catalysis by kinetics is due to the complexity of the heterogeneous catalytic process comprising such single processes as adsorption, chemical reaction and desorption of the reacting products, as well as the migration of molecules on the catalyst surface toward active centers. Among these processes, sorption decreases with an increase in temperature, while desorption, as well as diffusion, increases with an increase in temperature.<sup>33</sup> When the thickness of the adsorption layer is constant, it is proportional to the adsorbed gas mass and a slowing down of the process may have its source

only in the continuity of diffusion. However, if density is variable, diffusion may be retarded for two reasons: (a) an increase in the continuity of diffusion, and (b) an increase in the diffusion resistance. Further, the Nernst-Fick diffusion law postulates that the resistance to diffusion varies as a power of the concentration.

Fick's linear diffusion law applied to the diffusion of a gas within a metal has been expressed by the following equation:  $\frac{dS}{dt} = \Delta \frac{dc}{dx}$  where  $dS$  is the quantity of gas diffusing in time  $dt$ ;  $\frac{dc^2}{dx}$ , the concentration gradient, and  $\Delta$ , the diffusion constant. The rate of change of concentration at any point is  $\frac{dc}{dt} = \frac{dc^2}{dx^2}$ . The rate of diffusion is proportional to the concentra-

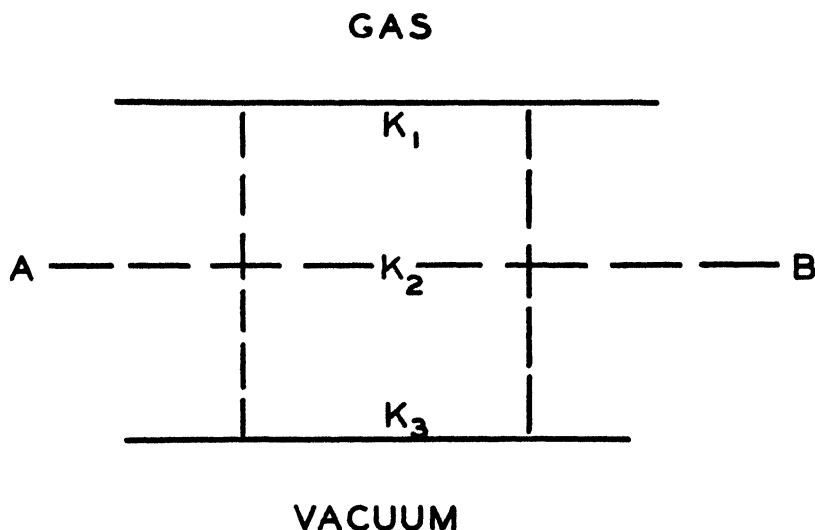


FIGURE 1.

tion gradient, but inversely proportional to the thickness of the metal. In Figure 1 a section through a sheet of metal is given. The line  $AB$  is a surface half-way through the metal. If the thickness of the metal is halved, the concentration gradient is doubled and likewise the rate of diffusion. The rate of diffusion increases very rapidly with temperature.

If a gas diffuses through a metal in the molecular state, the rate of diffusion should be directly proportional to the gas pressure or to the number of gas molecules striking the surface per second. Barrer,<sup>1</sup> also Braaten and Clark,<sup>5a</sup> studied the rate of diffusion of gases through glass and silica and found it directly proportional to pressure. Due to the very open spacing of the  $\text{SiO}_2$  lattice, it is a purely physical process. Air forced through a tube packed with kieselguhr gives a rate of flow proportional to the pressure. The rate of diffusion of gases through metals actually does not increase in a manner directly proportional to the pressure.

This is ascertained by plotting the rate of diffusion against pressure for several metals (Figure 2).

Diffusion is characterized principally by its velocity factor. Eckner<sup>7</sup> and Stefan<sup>37</sup> showed that the diffusion velocity varies inversely with the square root of the molecular weight. For the diffusion of gases through a layer, the following equation is valid:  $\frac{dm}{dt} = \frac{D}{\delta} (C_e - C_i)$ , in which  $\frac{dm}{dt}$  denotes the amount diffused per unit of time;  $D$ , the diffusion constant;  $\delta$ ,

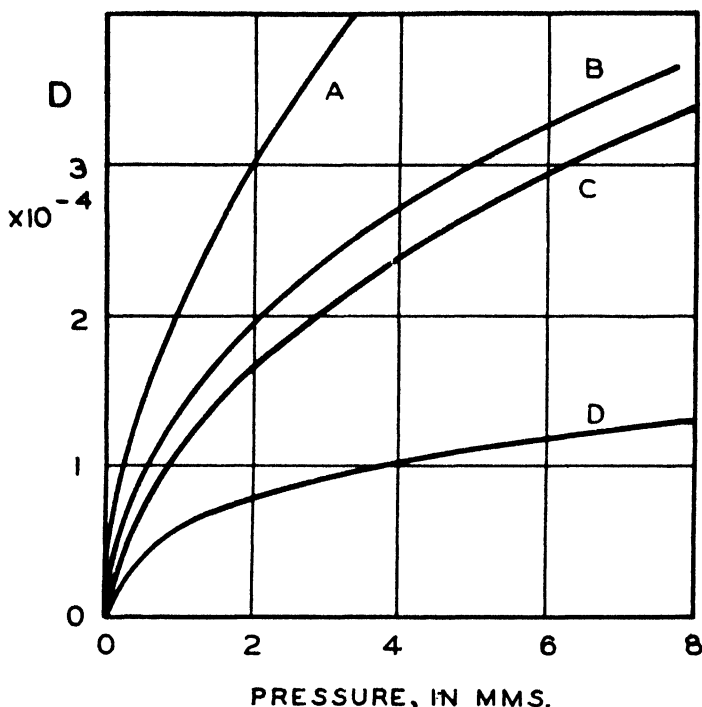


FIGURE 2.—Typical Diffusion Isotherms for Hydrogen.

- (A) Molybdenum at 1400°
- (B) Platinum at 1136°
- (C) Iron at 702°
- (D) Nickel at 587°

the thickness of the layer through which diffusion takes place, and  $C_e$  and  $C_i$ , the corresponding concentration of the gas at the external and internal surface of the layer.

Bodenstein and Fink, according to this law of diffusion, found that the reaction velocity in the catalytic oxidation of sulfur dioxide ( $2\text{SO}_2 + \text{O}_2 \longrightarrow 2\text{SO}_3$ ) is proportional to the velocity with which the slower diffusing gas ( $\text{SO}_2$ ) moves through the adsorption layer and that for the slower diffusing gas:  $\frac{dm}{dt} = \frac{D}{\delta} \cdot \alpha C_{\text{gas}}$  if the distribution equilibrium is:

$C_s/O_2 = \alpha_1 C_{gas}$  and  $C_s/2SO_2 = \alpha_2 C_{gas}$ . For  $C_i$  definite values are obtained only for the slower diffusing gas when  $C_i = 0$ . Thus:

$$\frac{dm}{dt} = D \cdot \alpha_2 \frac{[2SO_2]}{[2SO_3]^{1/2}} = K \cdot \frac{a-x}{x^{1/2}} = \frac{dx}{dt}$$

Schmidt,<sup>33</sup> in his analysis of (a) adsorption at the plane  $E_1$ ; (b) diffusion from  $E_1$  to  $E_2$ , and (c) desorption at the plane  $E_2$  occurring in diffusion through a thin membrane of rubber, pointed out that if the velocity of adsorption (process 1) is considered for higher concentrations, then the velocity of diffusion (process 2) is expressed, according to Fink's law, by the equation:  $\frac{dS}{dx} = D \frac{\partial e}{\partial x} \cdot q$ . By changing from the differential quotient to the difference quotient, he found the amount  $S$ , which diffused per unit of time, proportional to the cross section  $q$ , the concentration drop  $\frac{c_1 - c_2}{x}$ , and the diffusion constant  $D$  varying with the adsorbed gas. If the cross section  $q$ , the concentration potential  $\frac{c_1 - c_2}{x}$  and the temperature are kept constant, then  $D$  is approximately constant for the same adsorbent. The concentration at planes  $E_1$  and  $E_2$  in the equilibrium state is given by the laws of adsorption.

In case different pressures are involved, the concentration for pressures  $P_1$  and  $P_2$  is determined by the following equations:

$$C_1 = A \frac{P_1}{RT} e^{\frac{m'\sqrt{\lambda}}{RT}} \quad C_2 = A \frac{P_2}{RT} e^{\frac{m'\sqrt{\lambda}}{RT}}$$

$$C_1 - C_2 = A \frac{P_1}{RT} e^{\frac{m'\sqrt{\lambda}}{RT}} - A \frac{P_2}{RT} e^{\frac{m'\sqrt{\lambda}}{RT}}$$

or

$$S = A' \frac{P'}{RT} e^{\frac{m'\sqrt{\lambda}}{RT}}$$

which is interpreted, according to Schmidt, that diffusion under these conditions follows the same law as adsorption. If  $T$  and  $P^1$  are constant, then:  $\ln S = B \sqrt{\lambda} - C$ . The formula postulates that gases with higher  $\lambda$ , which corresponds to a higher boiling point, exhibit a greater tendency to diffusion than those with a lower boiling point.

Smithells and Ransley<sup>36a</sup> studied the effect of surface treatment on the diffusion of hydrogen through iron and nickel as shown in Table 5. The etching of the iron surface with dilute nitric acid, for example, increases the rate of diffusion ten times.

The rate of diffusion of hydrogen through iron may be increased ten to fifteen times by heating the metal in nitrogen.<sup>13a</sup> The rate of diffusion is greatly reduced if the metal is slightly oxidized. Palladium and some other metals are especially affected by preliminary heat treatment. Ham<sup>13a</sup> found that the rate of diffusion for fresh passive palladium fell to one-fiftieth of its initial value when heated for several hours at 1000°C.

Table 5.  
(Smithells and Ransley)

Metal	Treatment	Temperature (°C.)	Pressure (mm.)	Rate of Diffusion
Nickel.	Polished.	750	0.042	$1.39 \times 10^{-6}$
	Oxidized and reduced.	750	0.042	$2.70 \times 10^{-6}$
	Polished.	750	0.091	$2.91 \times 10^{-6}$
	Oxidized and reduced.	750	0.091	$4.23 \times 10^{-6}$
Iron.	Polished.	400	0.77	$0.47 \times 10^{-7}$
	Etched.	400	0.77	$4.4 \times 10^{-7}$
	Polished.	590	0.073	$1.28 \times 10^{-7}$
	Oxidized and reduced	590	0.073	$0.76 \times 10^{-7}$
	at 600°C.	590	0.073	$1.54 \times 10^{-7}$

Permeability is recovered by heating at 500°C. in oxygen, whereby an oxygen film is formed and then reducing it by treatment with hydrogen at 150°C. Heating in nitrogen increases the permeability of palladium. The rate of diffusion of hydrogen through nickel has been found by Baukloh and Kayser<sup>17</sup> to remain constant up to 850°C. and to fall off gradually at higher temperatures. At 1060°C. the rate fell to 30 per cent of the initial value after six hours.

According to Ramsey's interpretation, the fact that diffusion is not proportional to the pressure in the case of metals may be attributed not to the diffusion of molecular hydrogen, but rather to hydrogen in the atomic or dissociated state. However, Richardson showed that the rate of diffusion of hydrogen through platinum was much higher than could be accounted for by the dissociation of the gas. He assumed that the gas was completely dissociated inside the metal and was in equilibrium with molecular hydrogen outside the metal. From the law of mass action, Richardson deduced the equation:  $D = K \sqrt{p}$ , which was modified by Borelius and Lindblom:<sup>9</sup>  $D = K (\sqrt{p} - \sqrt{p_0})$ , and by Smithells and Ransley:<sup>36a</sup>  $D = K\theta \sqrt{p}$ , where  $\theta$  is the fraction of the surface covered by the adsorbed gas.

Investigating the diffusion of hydrogen through copper, iron, nickel, and molybdenum, as well as nitrogen through molybdenum, Smithells and Ransley proposed a new equation for diffusion:

$$D = K(ab \cdot P)/(1 + \alpha P)\sqrt{P}$$

This equation incorporates Langmuir's isotherm, which is in agreement with experimental results and interprets diffusion through adsorption of the gas on the surface.

Franzini<sup>9</sup> considered the deviation from proportionality between diffusion and  $P$  due to a threshold value of adsorption or evaporation pressure established for the diffusion of hydrogen through palladium. He assumed that molecules of an adsorption layer on a metal surface retained by electrostatic force caused a disturbance of electrons in the surface atoms which influenced diffusion through the metal lattice. Since the surface layer is in equilibrium with the gas phase, those factors which influence it also influence the diffusion of the gas. Experiments of Franzini show

that while  $H_2^2$  is adsorbed more readily than  $H_2^1$  on palladium,  $H_2^1$  diffuses more rapidly than  $H_2^2$ .

Ledoux<sup>18a</sup> describes an arrangement for measuring diffusion velocities. This consists of a large two-shank U-tube filled with mercury and in one of the shanks the gas may diffuse through a membrane under pre-determined super-pressure.

Kobosew and Monblakowa<sup>17</sup> considered the mechanism of hydrogen diffusion through palladium in the case of electrolysis a complex phenomenon which may be divided into three processes, namely, electro-diffusion, electro-occlusion, and electro-catalysis. They assumed that by converting a hydrogen molecule into a Me-H compound on the Me surface, a definite optimum value of binding energy,  $\psi_H$ , is attained, corresponding to the occlusion velocity. While the velocity in ordinary processes must decrease with a decrease in  $\psi_H$ , in accelerated or catalytic processes it should increase with a decrease in  $\psi_H$ . This behavior is reversed by factors influencing the adsorption potential  $\psi_H$ . These investigators proved experimentally that such behavior was the function of poisons. They also ascertained that electro-diffusion is not sensitive to changes in the physical properties of the medium in contact with the diffusion side of palladium; poisoning of the polarization side accelerates electro-diffusion, while poisoning of the diffusion side retards electro-diffusion. Bodenstein<sup>2</sup> found a definite proportionality between  $\log \beta$ , (change in diffusion velocity through poisoning) and the change in the hydrogen potential  $AE$  for hydrogen diffusion through an iron cathode. The velocity factor of electro-diffusion is strongly influenced by electrolytes, such as potassium chloride and potassium hydroxide. Kobosew and Monblakowa<sup>17</sup> approved for diffusion a definite mechanism connected with diffusion centers formed by crystal edges. Diffusion acts through a splitting within crystals.

The diffusion velocity is also a function of thermal pretreatment of the metal through which diffusion takes place. Ham and Sauter<sup>14</sup> considered this fact in their experiments on the diffusion of hydrogen through iron and palladium and ascertained for both metals that the law of mass action for diffusion is dependent on velocity only. If a fresh palladium preparation freed from gas gives a definite diffusion velocity at 300° and 760 mm. pressure, then a second palladium preparation might require a heating up to 600° at 760 mm. pressure in order to give the same value for the diffusion velocity. If iron is in contact with nitrogen, then the diffusion velocity of hydrogen may be ten to fifteen times greater; however, the diffusion curves coincide with their previous position when heated at higher temperatures. For very small velocities the diffusion isothermals of iron and palladium were found to correspond to a relationship approximately  $K_1 = A_1 \cdot p^{1.0}$ , while for very high velocities the expression changed to  $K_2 = A_2 \cdot p^{0.5}$ . The exponent changes continuously from one to the other.

Diffusion occurs readily from solutions. Graham employed the principle of diffusion of dissolved substances into a pure liquid medium to distinguish two groups of substances: colloids and crystalloids. In cases where a molecule is large in comparison to those of the solvent its diffu-



sion coefficient  $D$  may be calculated from the theoretically derived expression:  $D = \frac{RT}{N} \cdot \frac{1}{F}$ , in which  $F$  is the friction resistance;  $R$ , the gas constant equal to  $8.31 \times 10$ ;  $T$ , the absolute temperature ( $290^\circ$ ), and  $N$  equal to  $6.06 \times 10^{23}$  (Loschmidt's number). For a globule moving in a liquid, according to the laws of hydrodynamics,  $F = 6\pi\eta\rho$ , in which  $\eta$  is the viscosity coefficient and  $\rho$  the radius of the globule. Therefore,  $D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta\rho}$ .

From the theory of the Brownian movement it follows that colloidal particles should also diffuse, but to a much smaller extent than molecularly dispersed substances.

From this formula Svedberg concluded that the diffusion velocity is inversely proportional to the size of the dispersed particles. Picton and Linder illustrated the dependence of the diffusion velocity on the particle size by a series of arsenous sulfide sols included in the range between non-diffusible microscopically visible particles and diffusible microscopically invisible particles.

Table 6.

Solvated Colloids (1 $\mu\mu$ . diameter)	Coefficient cm. <sup>2</sup> /sec.
Amicronic gold sol.	$0.13-0.27 \times 10^{-5}$
(2-3 $\mu\mu$ . diameter)	
Albumins.	$0.01-0.08 \times 10^{-5}$
Egg albumen.	$0.06 \times 10^{-5}$
Urea.	$1.01 \times 10^{-5}$
Sucrose (cane sugar).	$0.57 \times 10^{-5}$

Whitman<sup>40</sup> considers diffusion as a process playing a major part in the interaction between phases and assumes it is restricted to molecular movement in a single phase without being aided by convection currents. The existence of a thin "stagnant" film is postulated at the boundary of any fluid and, on account of the absence of appreciable mass flow perpendicular to the surface, the material is moving through this film only by true diffusion. The thickness of such films varies from 0.001 cm. to 0.5 cm. The effective "film thickness" is determined primarily by the turbulence of the main body of the fluid adjacent to the film which in its turn is a function of velocity, density and viscosity. Whitman found that the effective film thickness determined for one set of conditions, for example, the adsorption of hydrochloric acid, could be used if another material, such as sulfur dioxide, was substituted under the same dynamic conditions. The coefficient  $R_g$  (proportionality factor for gas) is changed in proportion to the specific diffusion constant of sulfur dioxide as compared with that of hydrochloric acid.

Whitman<sup>21, 40</sup> reasoned that the rate of transfer of material per unit area is proportional to the potential difference between the main fluid and its surface, and that the potential difference is expressed as a difference in partial pressures when the phase is gaseous and as a difference of concentrations when it is liquid. He derived for the diffusion at the boundary surface of a gas the following rate per unit area:  $K_g(P_g - P_i)$ , and for

diffusion to the boundary of a liquid the rate per unit area:  $K_L(C_L - C_i)$ , where  $K_g$  and  $K_L$  represent proportionality factors for gas and liquid diffusion, respectively;  $P_g$  and  $C_L$ , pressure or concentration in the main fluid body, and  $P_i$  and  $C_i$ , pressure or concentration at the interfacial boundary. The proportionality factors  $K_g$  and  $K_L$  vary with the dynamic conditions of the system and the physical properties of the components.

The influence of diffusion in adsorption catalysis in gases, as well as in solutions, has been set forth by Freundlich<sup>10</sup> in the classification he proposed for adsorption combined with chemical processes occurring in the solid/gas interface and solid/liquid interface. He differentiated between inhibited and non-inhibited adsorption catalysis by the indirect influence of adsorption on the time-course of chemical reactions. Freundlich considered further that in non-inhibited adsorption catalysis the time-course of a true chemical reaction is not inhibited by diffusion, while in inhibited adsorption catalysis the time-course measured does not correspond to that of a chemical reaction, but involves a diffusion process occurring in the adsorption layer. In the latter case, inhibition may have another origin. It may be an inhibited adsorption catalysis in which one of the reacting substances initially present is concerned in the formation of a diffusion layer and therefore in the inhibition of diffusion, while the final products do not participate in this respect. Again, the end products of the reaction may be responsible for the diffusion layer and therefore for the inhibition of diffusion, while the initial components are ineffective. If a process consists of a number of successive stages, the velocity of the whole process is principally a function of the slowest component. Since diffusion proceeds slowly, it determines the velocity of the whole process of adsorption.

In the case of inhibited adsorption catalysis, Freundlich<sup>10</sup> considers the conditions still more complicated due to the fact that the diffusion layer is an adsorption layer; therefore the process is dependent on the diffusion of more than one gas. As an example of a case in which the observed velocity of the process is a purely chemical velocity at the surface and at the same time the velocity of diffusion, Freundlich gives the following catalytic reaction:  $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ . The velocity of the chemical adsorption reaction is very great. Of the three gases, sulfur trioxide has a very high critical temperature and therefore is readily adsorbed at high temperatures. If sulfur dioxide and oxygen combine at a reasonable rate at the surface of the platinum catalyst, then the sulfur trioxide layer will have an inhibitory action since the reacting substances, sulfur dioxide and oxygen, must diffuse through it. Oxygen diffuses more quickly, therefore diffusion of sulfur dioxide determines the velocity of the process.

Freundlich assumed that in general gas reactions are influenced by solid substances in such a manner that the velocity of the process is dependent only on a single reacting substance proportional to its first power. But, if it is inversely proportional to the first, or a fractional power of one of the reacting substances or end products, then the velocity of the process is governed by diffusion through an adsorption layer. Inhibition, evidence that the process is inversely proportional to the concentration of a reacting substance, may depend not only on the action of a diffusion layer, but

(Text continued on page 121)

Table 7. Inhibited Adsorption Catalysis (Solid/Gas Interface).

Reaction	Catalyst	Remarks
Decomposition of CO into CO <sub>2</sub> and carbon.	Nickel and cobalt surfaces	
Formation of CO <sub>2</sub> from CO and O <sub>2</sub> : $2SO_2 + O_2 \rightarrow 2SO_3$	Porcelain vessels V <sub>2</sub> O <sub>5</sub> , As <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , Cr <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> and SiO <sub>2</sub> .	Freundlich assumed that the rapid reaction of SO <sub>2</sub> and O <sub>2</sub> at the catalyst was due to adsorption catalysis rather than to the formation of intermediate compounds; with oxides of Fe and Cr, intermediate cpd. formation possible; with oxides of Al and Si, no intermediate cpd. formation impossible. According to Freundlich, CO inhibits its own combustion when it forms an adsorption layer through which oxygen diffuses; CO <sub>2</sub> may also be in the adsorption layer, but it does not influence the process.
Oxidation of CO by O <sub>2</sub> to CO <sub>2</sub> .	Quartz glass	At intermediate and lower temperatures.
$2SO_2 + O_2 \rightarrow 2SO_3$	Platinum.	
Catalysis of oxy-hydrogen mixtures.	Platinum	
Decomposition of NH <sub>3</sub> and SO <sub>2</sub> .	Quartz glass as adsorbent.	
Decomposition of nickel carbonyl: $Ni(CO)_4 \rightarrow Ni + 4CO$	Carbon monoxide has a strong inhibitory action, for it adheres and blocks the admixture of Ni(CO) <sub>4</sub> ; iron pentacarbonyl adsorbed by iron.	In addition to adsorption and diffusion, a displacement of reacting substances by reaction products takes place; this is very slow and causes a disturbance by clogging.

Table 8. Non-Inhibited Adsorption Catalysis (Solid/Gas Interface).

Reaction	Catalyst	Remarks
Decomposition of arsine (AsH <sub>3</sub> ), and phosphine (PH <sub>3</sub> ).	Solid reaction products accelerate.	Febly adsorbed gases, H <sub>2</sub> and N <sub>2</sub> , have no influence on the decomposition.
Decomposition of stibene. SbH <sub>3</sub> on solid antimony.	Finely divided antimony produced thereby acts catalytically on the reaction, the well-known S-shape curve of autocatalysis being obtained.	It is assumed that the catalytic action of Sb is due to the fact that SbH <sub>3</sub> is adsorbed on Sb; the equation for adsorption catalysis* shows that the reaction course is that of a chemical reaction.

- Schenck and Zimmermann: *Ber.*, **36**, 1231 (1903); Smits and Wolff: *Z. phys. Chem.*, **45**, 190 (1903).  
 Kuhl: *Z. phys. Chem.*, **44**, 385 (1903).  
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 Stoeffel: *Kolloid-Z.*, **12**, 59 (1913).  
 Van't Hoff: *Etude de dyn. Chim.*, **83**, (1884); Cohen: *Z. phys. Chem.*, **20**, 303 (1896); **25**, 483 (1898); Stock, Echeandia and Voigt: *Ber.*, **41**, 1319 (1908); Kooij: *Z. phys. Chem.*, **12**, 155 (1893); Trautz and Bhandarnar: *Z. anorg. allg. Chem.*, **106**, 95 (1919).  
 Bodenstein: *Ber.*, **40**, 570 (1907); Stock and Gutfmann: *Ber.*, **37**, 901 (1904); Stock, Grmolke and Heynemann: *Ber.*, **40**, 532 (1907).

Table 9. Inhibited Adsorption Catalysis (Solid/Liquid Interface).

Reaction	Catalyst	Remarks	Observer
Oxidation of oxalic acid by oxygen: $2(\text{COOH})_2 + \text{O}_2 \rightarrow 4\text{CO}_2 + 2\text{H}_2\text{O}$	Adsorbent, blood charcoal; inhibitors, methyl urethane, ethyl urethane and propyl urethane.	The inhibition by urethanes should be proportional to the amount adsorbed and hence depends, according to the adsorption isothermal, on the concentration of the solution; inhibition: $H = 100 \frac{V_0 - V}{V_0 - V'}$ ; $V_0$ , volume of $\text{O}_2$ adsorbed in 2 hours in the absence of urethane; $V'$ , that in the presence of urethane; oxalic acid strongly adsorbed forms a layer on the charcoal through which oxygen must first diffuse in order to react quickly with the acid on the surface of the charcoal. The final products, sulfur and Hector's base, are very difficultly soluble in water, and remain at the interface; and in all probability they exhibit the diffusion of oxygen more clearly than does phenylthiourea.	Warburg: <i>Pflüger's Archiv.</i> , 155, 547 (1914); Freundlich and Biercke: <i>Z. phys. Chem.</i> , 91, 31 (1916).
Oxidation of phenylthiourea by oxygen in an aqueous solution on blood charcoal.			Freundlich and Biercke: <i>Z. phys. Chem.</i> , 91, 1 (1916).

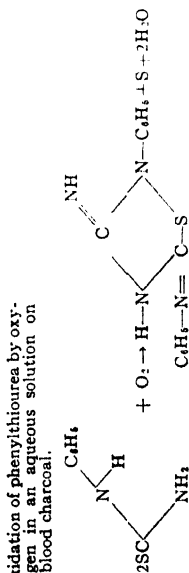


Table 10. Non-Inhibited Adsorption Catalysis (Solid/Liquid Interface).

Reaction	Catalyst	Remarks	Observer
Adsorption of $\text{AuCl}_3$ by charcoal: $4\text{AuCl}_3 + 6\text{H}_2\text{O} + 3\text{C} \rightarrow 4\text{Au} + 12\text{HCl} + 3\text{CO}_2$	Freundlich assumes the formation of an intermediate compound between gold and the silicate ion, an organic ion or a gold hydroxide which is then reduced by charcoal reacting similarly.	The adsorbent itself takes part in the reaction; the gold as a metal is found in the charcoal.	Avery: <i>J. Soc. Chem. Ind.</i> , 27, 255 (1908); <i>Graham Pogg Ann.</i> , 19, 143 (1830).
Adsorption of $\text{AgNO}_3$ and $\text{AgC}_2\text{H}_3\text{O}_2$ similar to that of $\text{AuCl}_3$ .	Rhodium contains oxygen or sulfur; the reaction proceeds best in a weak acid solution.	Only the adsorbed part of formic acid reacts.	Blackadder: <i>Z. phys. Chem.</i> , 81, 385 (1912).
Decomposition of formic acid by rhodium: $\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2$ .		Color changes to the yellow of the chromate; $\text{OH}^-$ ions enter the solution by exchange adsorption forming with $\text{CrO}_4^{2-}$ the $\text{CrO}_4^{+}$ ions; as shown by Orying, adsorption is followed by a further chemical reaction leading to the formation of $\text{Cr}^{III}$ ions in the solution and probably $\text{Cr}(\text{OH})_3$ on the adsorbent.	Ishizaka: <i>Z. phys. Chem.</i> , 83, 105 (1913); Orying: <i>Koll. Z.</i> , 13, 9 (1913).
Solution of $\text{K}_2\text{Cr}_2\text{O}_7$ on fibrous alumina as adsorbent.		Catalytic action proportional to the amount of active substance adsorbed. The velocity increases in proportion to the surface of platinum black.	Elissaff: <i>Z. Elektr.</i> , 21, 352 (1915).
Decomposition of $\text{H}_2\text{O}_2$ by glass wool (adsorbent and catalyst): Reaction between $\text{NaH}_2\text{PO}_4$ and $\text{H}_2\text{O}$ : $\text{NaH}_2\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{NaH}_2\text{PO}_3 + \text{H}_2$ .	Salts of heavy metals, such as Mn, Cu. Platinum black.		Sieverts and Peters: <i>Z. phys. Chem.</i> , 91, 199 (1916).

Table 11. Non-inhibited Adsorption Catalysis (Liquid/Gas Interface)  
(Adsorbed gas reacts with the adsorbent).

Reaction	Catalyst	Remarks	Observer
Combustion of freshly prepared wood charcoal.	Iron oxide.	Coal containing iron oxide explodes at low temp. upon adsorption of O <sub>2</sub> ; coal free from iron oxide does not.	Hargreaves: <i>J. Chem. Soc.</i> , <b>27</b> , 420 (1874); Wohler:
Taking up of oxygen by charcoal not possible adsorption; for carbon and oxygen yield carbon monoxide which is oxidized by oxygen into carbon dioxide.	Water		Baker: <i>J. Chem. Soc.</i> , <b>51</b> , 249 (1887); de Saussure: <i>Gill. Ann.</i> , <b>47</b> , 113 (1814); Lowry and Hueltet: <i>J. Am. Chem. Soc.</i> , <b>42</b> , 408 (1920); Dixon: <i>Ber.</i> , <b>38</b> , 2426 (1905).
Action of moist oxygen and charcoal. Decomposition of hydrogen selenide upon selenium surface.	Water. Selenium.	Intermediate product, formic acid.	Wieland: <i>Ber.</i> , <b>45</b> , 679 (1912).
Oxidation of liquid sulfur to sulfur dioxide.	Sulfur molecules.		Bodenstein and Fink: <i>Z. phys. Chem.</i> , <b>60</b> , 46 (1907). Bodenstein and Karo: <i>Z. phys. Chem.</i> , <b>75</b> , 30 (1911).

Table 12. Non-inhibited Adsorption Catalysis (Liquid/Gas Interface)  
(Two adsorbed substances react at the surface of the adsorbent).

Reaction	Catalyst	Remarks	Observer
Silicon hydride and oxygen.	Wall of the vessel as adsorbent.		Friedel and Ladenburg: <i>Lieb. Ann.</i> , <b>143</b> , 118 (1867).
Cl adsorbed on moist charcoal hydrolyzed to HCl.	Water; maximum velocity at 15°C and 30%; decrease at 35°C.	Oxygen generated unites quickly with carbon to form CO <sub>2</sub> .	Melsens: <i>Ann. Chim. Phys.</i> , (5), <b>3</b> , 522 (1874).
Decomposition of phosphine to HCl and CO <sub>2</sub> upon adsorption on charcoal.	Water.	Formation of phosphine from CO and Cl <sub>2</sub> when passed over charcoal.	Paterno: <i>Gazz. Chim. Ital.</i> , <b>5</b> , 233 (1875).
Synthesis of sulfuryl chloride from SO <sub>2</sub> and Cl <sub>2</sub> and its decomposition.	Charcoal.		Trautz: <i>Z. Elektro.</i> , <b>21</b> , 329 (1915).
Oxidation of H <sub>2</sub> S by O <sub>2</sub> to S and H <sub>2</sub> O.	Charcoal.		Freundlich: "Colloid and Capillary Chemistry," E. P. Dutton & Co., Inc., New York, 1922.
Hydrogenation of charcoal containing adsorbed Cl <sub>2</sub> to HCl which is freely developed.	Charcoal.		Berthelot and Guntz: <i>Compt. rend.</i> , <b>99</b> , 7 (1884).
Synthesis of phosphine and oxygen.	Wall of the vessel as adsorbent.	Explodes on expansion.	van de Stadt: <i>Z. phys. Chem.</i> , <b>12</b> , 322 (1893).
Oxy-hydrogen mixture.	Wall of a glass vessel.	Ignition temperature falls from 620° to 540° by reducing pressure from 76 to 36 cm. mercury; interpreted by Freundlich as dealing with two gases, one of which is oxygen or hydrogen (oxy-hydrogen mixtures have a considerably lower B.p. than other mixtures, for they cause a change in pressure and in the ratio of the amounts adsorbed; a ratio may be obtained for which the velocity of the reaction in the adsorption space is greater than that with the higher pressures at first present).	Mitscherlich: <i>Ber.</i> , <b>26</b> , 399 (1893).
Oxidation of aldehyde by O <sub>2</sub> .	Wall of the vessel as adsorbent.	Maximum effect when the conc. of the one adsorbed substance increases.	Ewan: <i>Z. phys. Chem.</i> , <b>16</b> , 315 (1895).

also on the principle of displacement.<sup>26, 27</sup> According to Reichenstein, if the velocity of reaction of substance *B* present in excess at the surface, which depends not only on the pressure in the gas space but also on adsorption, increases with an increase in the amount of substance *A* adsorbed, then the displacement of *B* caused thereby will be negligible, but as soon as *A* assumes values at the surface, a considerable displacement of *B* takes place, and the velocity finally decreases because *B* is present at the boundary surface in ever decreasing amounts; at a definite ratio of *A* to *B*, the velocity will reach its maximum.

Data for inhibited and non-inhibited adsorption catalysis in the solid/gas interface, taken from Freundlich's classification, are presented in Tables 7 and 8. (page 118).

Freundlich applied the same classification of adsorption catalysis to the solid/liquid interface, examples of which are summarized in Tables 9 and 10. (page 119).

Table 11 (page 120) shows non-inhibited adsorption catalysis reactions in the liquid/gas interface in which the adsorbed gas reacts with the adsorbent, and Table 12 (page 120) shows two adsorbed substances reacting at the surface of the adsorbent.

Ward,<sup>39</sup> investigating the adsorption of hydrogen on copper, considered the slow reversible adsorption to be due to lattice or intergranular diffusion. Benton and White<sup>1</sup> and Taylor have shown that at low temperatures adsorption on metal and metal oxide catalyst reaches equilibrium within a few minutes. For diffusion of gases into the catalyst at low temperatures, it is possible to reach equilibrium within a short period of time, but for higher temperatures, the diffusion effect is questioned. However, these investigators assume that at low temperatures adsorption is limited to the external surface and to the large capillaries of the layer, while at high temperatures, due to an increase in molecular mobility on the surface, diffusion occurs in the intergranular spaces. They also state that at very low temperatures adsorption is not instantaneous, although such is the case at high temperatures.

Garner<sup>11</sup> considered the theory that the rate of activated adsorption is governed by the rate of diffusion as inapplicable and recommended the necessity for defining an "activated" type of diffusion, if the slowness of the rate is assumed to be due to diffusion. For normal diffusion processes, the rate increases as  $\sqrt{T}$ . Ward has shown that the rate of diffusion at constant temperature is proportional to the amount adsorbed on the accessible surface, but is not proportional to the gas pressure. The diffusion into the interior of the catalyst takes place when passing through the adsorption space, as would be the case if the capillaries were the size of molecules. Garner, considering the results of Knudsen's<sup>18</sup> rates of diffusion in capillaries the diameters of which were less than the free mean path of the gas molecules which do not conform to the law applicable to high pressures, postulates for activated diffusion the mechanism of a surface flow. Garner deduced that the rate of flow along the capillary is inversely proportional to the time in which molecules remain adsorbed at one spot. He assumed the surface concentration to be equal to:

$k \cdot p \cdot e^{-(Q-E)/RT}$ , where  $e^{-E/RT}$  and  $p \cdot e^{Q/RT}$  is proportional to the fraction of activated atoms and  $Q$ , the heat of adsorption. The rate of activated diffusion is, therefore, proportional to  $e^{-E/RT}$  and the activation energy of diffusion is that of activation of surface atoms. Garner apparently proved that the additional energy required for activation is supplied by surface atoms or that the surface atoms are those that are activated.

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### THE ENERGY FACTOR IN CONTACT CATALYSIS

In adsorption processes the energy levels of molecules or atoms composing the adsorbent undergo changes. The mechanism of adsorption catalysis in its turn is intimately related to the interplay of energies involved in it. To account for the energy involved in catalytic adsorption processes, single components composing the total heat effect must be considered. These are: (a) heat of adsorption corresponding to energy

liberated as heat when adsorption takes place; (b) various heats of the chemical reaction occurring on the adsorbent, such as heat of formation, heat of dissociation, etc., and (c) heat of activation which is closely related to the rate of a reaction and is used in estimating the catalytic effect. Each of the heat effects is subject to its own laws and there is also a definite interrelationship between them, depending upon variations in physical conditions under which this or that adsorption catalysis takes place. The order of magnitude of heat values changes, depending on the temperatures involved. It should be of help in formulating a general concept on energy values in adsorption catalysis to refer to single types of heat energies. The general feature of any chemical process in regard to energy evaluation of the reacting system is its classification into potential and kinetic energy.

Since the potential energy is rather a complex value composed of vibrational and rotational energies, as well as the electronic levels of molecules all of which are of different magnitude, the heat of adsorption has been considered as an algebraic sum of various changes in energy corresponding to relations existing between the adsorbent and the molecular fields of the adsorbate. There is one physical factor, temperature, which reflects its mutual influence upon the potential energy components and those of the adsorption heat. It is recognized experimentally that when adsorption occurs at low temperatures changes in the rotational and translational kinetic energy take place, while the potential energy is less affected. Increase of temperature in adsorption processes introduces new components in the energetic effect, namely, successive changes occurring in the vibrational energy and in the electronic levels. The existence of a great interval separating rotational, vibrational-rotational, and electronic-vibrational-rotational levels introduces assumed discontinuous changes in the liberated heat or heat of adsorption. From the above, it appears plausible that heat of adsorption is related to potential energy, while heat of activation is characteristic of kinetic energy.

### Heat of Adsorption

A rise in temperature during adsorption processes was observed by deSaussure,<sup>78</sup> Mitscherlich,<sup>63</sup> Favre,<sup>20</sup> Chappuis,<sup>9</sup> Bitter,<sup>7</sup> and others. Early observations established the fact that adsorption decreases with increase in temperature and may be accompanied by development of heat. Heat of adsorption may be defined as a change in the total energy by a reversible isothermal adsorption of one gram-molecule of a surface-active substance by a surface layer from a very large volume of a solution having a definite concentration.

Freundlich<sup>23</sup> was the first to formulate equations for the heat of adsorption and to differentiate two kinds of adsorption heats: (a) the integral heat of adsorption considered similar to the heat of solution that evolved when a gas is brought into contact with an adsorbent that takes it up until atmospheric pressure is reached (the majority of measurements on adsorption heats deal with the integral heat of adsorption), and (b) the differential heat of adsorption is the heat evolved when the process takes



place under equilibrium conditions. The amount adsorbed must not change appreciably either the pressure of the gas or the quantity of the material adsorbed.

Eucken<sup>18</sup> and Polanyi<sup>69</sup> considered the heat of adsorption equal to the adsorption potential, *i.e.*, the amount of work involved in bringing a mole of gas from an infinite distance to the surface.

Lorentz and Lande<sup>53</sup> deduced the equality between the adsorption potential and the heat of adsorption from the theorem of corresponding states. Their conclusion is valid only in regions where Henry's law holds true. Polanyi's equation for heat of adsorption refers to a gas in an uncondensable region. The equations for heat of adsorption were related to the second law of thermodynamics and varied, depending upon the conditions under which the experiments, mathematically accounted for, were performed. Williams<sup>95</sup> pointed out that these conditions may involve: (a) the vapor phase in equilibrium with the adsorbed phase,  $h/T$ ; (b) gas adsorbed at constant pressure,  $h/pT$ , and (c) gas adsorbed at constant total volume of the system  $(h)_vT$ . The following expressions for heat of adsorption may be found in the literature:

$$h = K_1 X^{K_2} \quad \text{Lamb and Coolidge}^{47}$$

$$h/pT = (h)_v T + RT$$

$$h/pT = RT^2 \left[ \frac{\delta \log p/P}{\delta \log T} \right]_x \quad \text{Williams}^{95}$$

$$H = K \cdot QT_e \quad \text{Lorentz and Lande}^{53}$$

$$Q = \frac{K}{T_e}$$

where  $K$  is the constant in the adsorption equation. The Clapeyron equation combined with Bertrand's vapor-pressure equation resulted in that of Homfray:<sup>37</sup>

$$h/pT = \frac{100 \times T}{T - x}$$

where  $x$  is the amount of adsorbate expressed in per cent of the adsorbent, and  $h$ , the heat of adsorption.

The total heat of adsorption is related to the adsorption potential:

$$H = E_x + \sigma x + \lambda \quad \text{Polanyi}^{69}$$

where  $\sigma x$  is the molar heat of compression;  $\lambda$ , the latent molar heat of evaporation, and  $E_x$ , the adsorption potential. Polanyi's theory postulates a compression of the gas on the surface of the adsorbent.

$$-H = E_s - E_i + \lambda_s \quad \text{Harkins and Ewing}^{31}$$

where  $H$  is the heat of adsorption of vapor sufficient to form a liquid layer covering the solid surface;  $\lambda$ , heat of evaporation;  $E_s$ , the total surface energy of the solid, and  $E_i$ , the total energy of the interface.

$$H = \frac{E_o^2}{8\pi} \left[ \frac{\epsilon - 1}{\epsilon} \right] \quad \text{Iliin}^{38}$$

where  $E_o$  is the tension of the electrical field *in vacuo*, and  $\epsilon$  the dielectric constant of the adsorbed gas.

$$\frac{d \ln P}{dT} = \frac{\lambda}{RT^2} \quad \text{Gauger and Taylor}^{29}$$

$$\lambda = 1.99 \times 2.303 \frac{T_1 - T_2}{T_2 - T_1} \log \frac{P_2}{P_1}$$

where  $\lambda$  is the heat of evaporation;  $P$ , the saturation pressure, and  $R$ , the gas constant = 1.99 cal.

$$Q = W - T \frac{\partial W}{\partial T} \quad \text{Rehbinder}^{76}$$

The heat of adsorption is determined as the change in the total energy in a reversible isothermic adsorption of one gram-molecule from the surface layer and is derived from the general equation of thermodynamics which related the work of the isothermic reversible process  $W$  with the heat effect  $Q$ .

$$q = \int_0^{\text{total}} \epsilon \frac{dx}{x} \quad \text{Dixon}^{12}$$

The heat of adsorption  $q$  in calories per mol adsorbed is expressed in terms of the adsorption potential  $\epsilon$  and the amount adsorbed  $x$ . The integral is evaluated graphically by plotting  $\frac{\epsilon}{x}$  versus  $x$  and measuring the area under the curve.

### Differential Heats of Adsorption

The expression for the differential heats of adsorption under isosteric conditions (when transformations from one equilibrium condition to another take place with the amount of the adsorbate practically constant at different pressures and temperatures) was derived by Freundlich from the Clapeyron and Clausius equation:

$$-h_x = \frac{hRT^2}{22410 \log_{10} e} [\zeta - \xi \log p]$$

where  $x$  is the constant and  $p$  the variable. The isosteric heat of adsorption  $h_x$  corresponds to the heat of evaporation  $q_a$ . The equation:  $x = xp^{1/r}$  is obtained from

$$\begin{aligned} d \frac{\log p}{dT} &= \frac{n}{\log_{10} e} [\zeta - \xi \log_{10} p] \\ -q_a &= \frac{RT^2}{22410} \cdot d \frac{\log p}{dT} \end{aligned}$$

where  $1/n$  is the adsorption exponent and  $\zeta$  and  $\xi$  are temperature coefficients for the heat of evaporation.

Freundlich cites another example of differential heats of adsorption where the pressure is kept constant and the adsorbed amount changes

with the temperature at a given pressure. This heat of adsorption is the isobaric heat corresponding to the heat of the reaction in a condensed system. Heats of adsorption may range from small values differing not greatly from those of heats of liquefaction to quite large values. In the adsorption of gases on active catalysts, quite large heat effects are obtained.

Beebe and Taylor<sup>5</sup> described a method for direct measurement of heats of adsorption of carbon monoxide on copper catalyst. The integral values were calculated from the average of the differential values, these differential values being found much higher for the initial portions of carbon monoxide adsorbed than for the later portions, and they were never less than 8,000 calories.

Taylor (G. B.),<sup>82c</sup> Perry, Kistiakowsky and Taylor (H. S.),<sup>68</sup> and Kistiakowsky, Flosdorf and Taylor (H. S.)<sup>42</sup> measured differential heats of adsorption of hydrogen on zinc oxide-chromic oxide catalyst, as well as of oxygen on platinum. Decided maxima in curves were obtained for the adsorption of hydrogen on zinc oxide-chromic oxide catalyst, but no maxima in curves were obtained for the adsorption of oxygen on platinum. There is a difference in opinion as to the interpretation of these maxima. Taylor considered high adsorption heats due to factors other than the impurities in the adsorbent influenced by the velocity of removing gases from the adsorbent.

Garner and Blench,<sup>26</sup> Garner and McKie,<sup>28</sup> and Keyes and Marshall<sup>39</sup> determined the differential heats of oxygen adsorbed on charcoal as ranging from 19,000 in the initial stages of adsorption to 4,000 calories close to the saturation point. Such a magnitude of potential energy change has been considered as indicating a chemical combination of the adsorbed molecule with the surface.

Magnus, Sauter and Kratz,<sup>56</sup> studying the adsorption of carbon dioxide by charcoal, obtained data for differential heats of adsorption of carbon dioxide on purified charcoal indicating that these were constant in the low pressure region (up to 3 mm.) and considered that this was due to the removal of oxide impurities. The adsorption isotherm of carbon dioxide was found to be superimposed by a sorption isotherm of carbon dioxide on the oxide impurities. The adsorption heat of carbon dioxide on pure coal lies between 7,000 to 8,000 calories, while the sorption heat of carbon dioxide on the oxide impurities is of the order of 20,000 and 30,000 calories. Sauter<sup>79</sup> considered it probable that high heats of adsorption, especially differential heats, may be evidence that a "chemical sorption" rather than a "pure adsorption" has taken place. Therefore, stable surface compounds are formed with liberation of much energy. McKie<sup>61</sup> and Marshall and Bramston-Cook<sup>58</sup> also emphasized the fact that the heat of adsorption of oxygen is changed on account of a chemical reaction between it and charcoal.

Magnus and Kieffer<sup>55</sup> state that although water is extremely difficult to remove from an adsorbent, it does not seem to affect greatly the amount of heat adsorbed.

Taylor, Kistiakowsky and Perry,<sup>87</sup> measuring the differential heats for oxygen on platinum black free from other adsorbed substances, such

as water or hydrogen (with which oxygen may react chemically), obtained values decreasing from 78,000 to 3,000 calories per gram-mol with an increase in the concentration of the adsorbate. On the other hand, Maxted and Hassid's<sup>60</sup> curves indicated a constant differential heat of adsorption for copper and platinum throughout the whole range of hydrogen concentration. The constant heat of adsorption was about 33,000 calories per gram-mol of hydrogen.

Table 1.

Total Hydrogen Adsorbed (cc.)	Differential Heats of Adsorption (cal./mol Hydrogen)
0.57	16,600
1.10	16,500
1.73	15,800
5.20	16,000
13.00	17,200
16.00	17,200

Contradictory results were obtained for the dependence of the differential heats of adsorption on the stage of adsorption. Fryling<sup>24</sup> produced evidence supporting the fact that the differential heat of adsorption for hydrogen per gram-mol on nickel (function  $dQ/dc$ , where  $Q$  is the heat evolved and  $c$  the concentration of the adsorbed hydrogen) increased from a low value to a maximum of 32,000 calories per gram-mol of adsorbed hydrogen with an increase in the hydrogen concentration.

On the other hand,<sup>41, 43</sup> an increase to a maximum followed by a decrease in the differential heat was observed for an increase in the concentration of hydrogen adsorbed by copper and the maximum heat of adsorption amounted to 18,000 calories per gram-mol. A great variation of the maxima obtained for differential heats of adsorption for hydrogen, for example, was established for various specimens of metals. It also appears that a specimen of a metal of relatively high catalytic activity has a higher differential heat of adsorption than an overheated and less active specimen.

Table 2. Hydrogen Adsorption.

Metal	Maxima of Differential Heats (calories)	Observer
Platinum.	32,400	Taylor, Kistiakowsky and Perry. <sup>87</sup>
Nickel.	12,000-37,000 32,000	Maxted and Hassid. <sup>60</sup> Fryling. <sup>24</sup>
Copper.	18,000	Kistiakowsky, Flosdorf and Taylor. <sup>42</sup>
Silver.	Very low	Maxted and Hassid. <sup>60</sup>

Taylor, Kistiakowsky and Perry,<sup>87</sup> using a very active platinum obtained by reduction of platinum chloride with formaldehyde, obtained very high values for the adsorption heat of hydrogen, sulfur dioxide and carbon monoxide, about 30,000 calories, while for oxygen at 0°C., the values per mol oxygen adsorbed ranged between 104,000 to 161,000.

Washburn<sup>94</sup> studied the adsorption heats of hydrogen, ethylene and ethane and found the following:

Table 3.

Gas	Adsorption Heats (cal./mol at 0°C.)
Hydrogen.	11,300
Ethylene.	16,000
	17,300 (on Ni) <sup>81</sup>
Ethane.	11,000

Pearce and Reed<sup>66</sup> investigated adsorption heats of methyl chloride, isopropyl chloride and secondary and tertiary butyl chloride vapors at 25° and 50° and ethyl and propyl chloride vapors at 50° on active charcoal and found that in general adsorption heats derived theoretically are lower than those obtained experimentally. The equation  $\log h = \log m + n$ , gave good agreement, where  $h$  is the number of calories, and  $X_{cm}^3$  vapor adsorbed by one gram of coal. Both variables,  $m$  and  $n$ , are somewhat dependent on temperature for each organic vapor. The adsorption heat does not increase with increasing temperature, as in the case of oxygen where a chemical reaction superimposes the adsorption phenomenon to a greater extent at higher temperatures. The total adsorption heat of an organic vapor increases apparently linearly with the total value of the adsorbate. The molar heat of adsorption of vapors was found to be smaller for substances having a branched chain than for compounds with a straight chain; for the normal compound, the molar adsorption heat increases with the length of the chain. High heats of adsorption are found not only for metal catalysts, but also for metallic oxides.

Table 4. Differential Heats of Adsorption for Hydrogen on ZnO - Cr<sub>2</sub>O<sub>3</sub>.

Hydrogen		Adsorption Heat per mol Hydrogen Adsorbed	Observer
Adsorbed	Unadsorbed		
0.237	0.003	21,200	Flösdorf and Kistiakowsky: <i>J. Phys. Chem.</i> , <b>34</b> III, 1907 (1930).
0.225	0.009	25,000	
0.222	0.018	25,300	
0.224	0.021	26,300	
0.215	0.025	28,800	
0.210	0.030	30,800	
0.200	0.033	27,400	

Maxted,<sup>59</sup> studying the differential heat of adsorption of hydrogen on platinum at 0° and 20°, claimed that the differential heats of adsorption pass through well-defined maxima which, on ageing of the catalyst, become less pronounced. Taylor and Kistiakowsky<sup>66a</sup> have pointed out that the heat of adsorption changes with time. It is much less at the end of the time interval when the entire surface is filled up. Maxted also emphasized the fact that differential heats of adsorption are specific for the conditions and pretreatment<sup>67</sup> of the catalyst and that high catalytic activity is related to a high differential heat of adsorption. Taylor illustrated the significance of values of differential heats for catalytic activity by Dew's observations for the adsorption of ammonia on copper, nickel, and iron, indicating that all the adsorption heat curves run parallel and that the adsorption heat of iron is greater than that on nickel by 5,000 calories and greater than that on copper by 7,000 calories. Taylor deduced further under the assumption that the activation energy is the same for all three

contact masses, that the reaction velocity on iron is faster than on nickel in the ratio of  $e^{\frac{5000}{RT}}$  :1, and faster than on copper by  $e^{\frac{7000}{RT}}$  :1. At 800° absolute temperature, the ratio of the reaction velocities is 20:1 and 90:1. The velocity on iron would be faster than on a non-specific adsorbent in the ratio of  $e^{\frac{16000-6000}{RT}}$  :1, or at 800° absolute temperature,  $e^{6.25}$  :1.

Taylor attempted to correlate the differential heat of adsorption curves with surface catalytic activity.

The measurements by Pease<sup>67</sup> and Kistiakowsky, Florsdorf and Taylor (H. S.)<sup>43</sup> on the heat of adsorption of hydrogen on active and heat-treated copper catalysts showed that active adsorbents have maxima in curves (expressing heat of adsorption plotted against amount adsorbed); with partially de-activated catalysts, the maximum is present only for small amounts of the adsorbed gas, further de-activation eliminating it (Table 5).

Table 5. Differential Heats of Adsorption.

Adsorbent	Gas	Adsorption Heats (calories)	Observer
coal	sulfur dioxide	21,000	Polanyi and Welke: <i>Z. phys. Chem.</i> , <b>132</b> , 371 (1928).
silicic acid	sulfur dioxide	13,000	Magnus and Kieffer: <i>Z. anorg. allg. Chem.</i> , <b>179</b> , 216 (1929).
silicic acid	ammonia	12,000	

Table 6 expresses the variation in heats of adsorption for various gases and, at the same time, for various metals.

Table 6. Differential Heats for Hydrogen, Ammonia and Carbon Monoxide.

Catalyst	Gas	Average Adsorption Heats (calories)	Pressure Interval (mm.)	Observer
nickel	hydrogen	14,960	0-760	Dew and Taylor: <i>J. Phys. Chem.</i> , <b>31</b> , 297 (1927).
	ammonia	11,240	0-90	
copper	hydrogen	9,600	0-760	Beebe and Taylor: <i>J. Am. Chem. Soc.</i> , <b>46</b> , 45 (1924).
	carbon monoxide	30,000	0-1	Beebe and Taylor: <i>J. Am. Chem. Soc.</i> , <b>46</b> , 45 (1924).
	carbon monoxide	11,700	0-760	Beebe: <i>J. Phys. Chem.</i> , <b>30</b> , 1538 (1926).
	ammonia	9,200	0-155	Dew.
iron	ammonia	16,000	0-10	Dew.

### Integral Heats of Adsorption

Beebe and Taylor<sup>5</sup> showed that the integral heat of adsorption of hydrogen on nickel and copper was of the order of 10,000 to 20,000 calories, which was greatly in excess of the heat of liquefaction (450 calories for hydrogen) and varied with varying preparations of the catalyst.

Beebe<sup>4</sup> investigated the integral heat of adsorption of carbon monoxide on copper catalyst, as well as the effect of accidental poisoning (resulting in decreased adsorptive capacity) upon the integral values for heats of adsorption. The values for active copper were 11,700, 11,200 and 12,200 calories per mol, while the poisoned copper showed a marked increase in the integral heat of adsorption, 15,300 calories per mol.

Measurements of integral adsorption heats of carbon dioxide on coal

obtained by Magnus and Kälberer<sup>54</sup> by extrapolating to  $p = 0$  of the almost linear part of the adsorption heat curve gave  $Q = 7,450$  calories. The investigations of Magnus and Giebenhein<sup>53a</sup> showed that in the course of the linear carbon dioxide isotherm the integral adsorption heat assumes a constant maximum value and that the curve for the true adsorption heat has a different course in the low-pressure region. This Magnus interpreted by assuming that at low pressures the influence of unsaturated places of the adsorbent is so small that greater influence upon adsorption heat is exercised by the temperature factor. For carbon dioxide adsorption on carbon, the temperature at which practically no more adsorption takes place lies around  $400^\circ$ .

Table 7. Values for Integral Heats of Adsorption.

Adsorbent	Gas	Integral Heats (calories)	Observer
	argon	2,500	Kalberer and Schuster: <i>Z. phys. Chem. (A)</i> , 141, 270 (1929).
	nitrogen	2,900	
	ethylene	7,300	
silica gel	carbon dioxide	7,500	Magnus and Kalberer: <i>Z. phys. Chem. (A)</i> , 142, 40 and 41 (1929).
	hydrogen	500	
	ammonia	12,000	Magnus and Giebenhein: <i>Dissertation (Frankfurt a/M)</i> (1929).

To the value of the integral adsorption heat should always be added that of the linear part of the isotherm (where the unsaturated places do not have a predominant influence).<sup>79</sup> Heats of adsorption measured at low temperatures (between  $-180^\circ\text{C.}$  and  $-80^\circ\text{C.}$ ) by Benton and White<sup>8</sup> for hydrogen on metals, and by Langmuir<sup>19</sup> and Bawn<sup>3</sup> for gases adsorbed on mica, ranged between 500 to 2,000 calories. These heats are of the order to be expected from changes in potential energy attributed to the influence of van der Waals' forces acting between normal surface atoms and normal adsorbed molecules.<sup>50</sup> Heats of adsorption at room temperature show rather high values for small amounts adsorbed.

The heat of adsorption of water on platinum was calculated from the heat of adsorption of oxygen on the metal, and the heat of reaction of hydrogen with the adsorbed oxygen; the result was 5,500 calories. The heats of adsorption obtained for irreversible adsorption of oxygen on charcoal were found to be much larger than those for reversible adsorption. Garner<sup>25</sup> considers this accidental because irreversible chemical change does not necessarily take place with a very large heat of reaction.

Table 8. Irreversible Adsorption.

Adsorbent	Gas	Heat of Adsorption (calories/Mol)	Observer
charcoal	oxygen	72,000	Garner: <i>J. Chem. Soc.</i> , 125, 1288 (1924); 2451 (1927).
		227,000	
tungsten	oxygen	160,000	Garner and Blench: <i>J. Chem. Soc.</i> , 125, 1288 (1924). Langmuir and Kingdom: <i>Phys. Rev.</i> , 24, 570 (1924).

Garner<sup>25</sup> classifies processes with heat of adsorption ranging from 19,000 in the initial stage of adsorption to 4,000 calories close to the saturation point into those with reversible and those with irreversible

changes. Reversible changes are those in which the adsorbed molecules can be recovered completely by desorption, while in irreversible changes there may be a chemical combination of the adsorbed gas with the adsorbent.

High-temperature adsorption results in heats of adsorption lying between 10,000 and 30,000 calories per mol and more. In addition to this, these processes possess quite a large critical increment.<sup>85</sup> Polanyi and Wigner<sup>74</sup> expressed the relationship between the rate of the surface reaction and the observed critical increment as follows:  $\frac{-dx}{dt} = AnVde^{-E_o/RT}$ , where

$A$  is the area of the surface;  $n$ , the number of molecules per cc. of gas;  $d$ , the thickness of the adsorption space (about  $10^{-8}$  cm.);  $E_o$ , the observed critical increment, and  $V$ , the frequency of vibration of the adsorbed molecule.

Polanyi<sup>70</sup> derived a formula relating to the observed critical increment  $E_o$ , the critical increment of molecules in a gaseous phase  $E_q$ , and the heat of adsorption  $Q_A$ , which reads:  $E_o = E_q - Q_A$ . This equation holds provided the rate of adsorption is much more rapid than the rate of chemical change. Foresti,<sup>22</sup> studying the adsorption of hydrogen on nickel, found no increase in the heat of adsorption with a decrease in the adsorption capacity. Taylor<sup>85</sup> found that the heat of adsorption  $Q_A$  increases as the degree of saturation of the surface decreases.

Hinshelwood and Burk,<sup>35</sup> investigating the decomposition of ammonia on tungsten, found the critical increment to be 38,700 calories for 900° to 1600°, and Kunsman<sup>46</sup> reported it as 35,000 calories at 1000° to 1250°, and 45,000 calories at 800° to 1000°. Hailes,<sup>30</sup> studying the thermal dissociation of ammonia on tungsten, established the fact that the critical increment varies with the pressure; he obtained 31,060 calories for 3.7 cm. pressure of ammonia, and 26,800 calories for 0.7 cm. pressure and a temperature range from 950° to 1150°. This decrease in the critical increment was explained as due to an increase in the heat of adsorption of ammonia as the gas pressure decreased.

Many investigators have sought to link the order of magnitude of adsorption heats to the properties of the adsorbent. It has been recognized that heats of adsorption at room temperature are sometimes dependent on the number of gas molecules adsorbed per unit area of the surface, while in many other cases it has been proved that heat of adsorption is independent of the surface covered.<sup>60, 93</sup> Taylor and Kistiakowsky<sup>86a</sup> pointed out that in places where atoms possess greatest freedom the heat of adsorption may be almost equal to the heat of the chemical reaction between the adsorbent and the adsorbate. Much consideration has been given to the possibility of relating increased adsorption potential or high heats of adsorption with the existence of active places on the adsorbing catalytic surface.

Taylor formulated Langmuir's conceptions into a general theory of active surfaces and ascribed a strong increased adsorption potential to the unsaturated active places of the surface. The modified theory of gas



adsorption of Langmuir<sup>49</sup> postulated that a surface shows various types of elementary spaces on some of which activation, as well as adsorption, of the gas molecules may occur, whereas on the remaining part adsorption alone takes place. The experiments of Pease<sup>67</sup> with metallic catalysts seem to confirm the viewpoint that if catalytic surfaces are considered as having variable elementary spaces, then adsorption on the most active elementary spaces is accompanied by an activation process; in other words, there is a dependence of activation and heats of adsorption on the nature of the catalyst surface.

Somewhat similar was the deduction made by Beebe<sup>4</sup> from a study of the integral and differential values of heat of adsorption of hydrogen for "active" and "poisoned" samples of copper and nickel catalyst. His results indicate the fact that the catalyst surface contains copper atoms at various energy levels and that those of the highest level are the first to adsorb the incoming gas molecules, while other points of low energy level either fail to adsorb or fail to distort the electronic configurations of the reactants, which are sufficient to bring about their combination. Therefore Beebe's viewpoint was in conformity with the theory that points of highest degree of unsaturation on the metal surface are seats of catalytic power. Beebe also found that the integral value of heats of adsorption was about 20 per cent higher for the "poisoned" (with carbon monoxide) catalyst than for the "active" sample. The effect of poisoning seems to produce evidence that points on the copper surface deprived of their adsorptive capacity were not those of a high energy level.

Taylor and Kistiakowsky,<sup>86a</sup> on the basis of their theory, assumed that only a part of the surface atoms, namely, those which are highly unsaturated, activate the adsorbed gas molecules as indicated by measurements of the dependence of the adsorption heat on the degree of saturation of the surface, and pointed out that the process is endothermic for: (a) hydrogen on active copper; (b) hydrogen on copper poisoned with oxygen, and (c) carbon monoxide on active copper. The three different curves obtained were considered a logical consequence of the above theory. Further, it appeared to Taylor and Kistiakowsky that places on the surface of a catalyst having greater heats of adsorption possess greater chemical activity. Taylor<sup>82c</sup> assumed that the activation energy is constant and deduced from adsorption heats that only the parts of the surface corresponding to active places which adsorbed the first 4 cm.<sup>3</sup> of gas are of importance for the reaction velocity. The reaction velocity was found to be reduced to 28 per cent of the normal when a poison covered the surface which otherwise is covered by the first cm.<sup>3</sup> of the gas. Pease stated that in his experiments 0.2 cm.<sup>3</sup> carbon monoxide decreased the hydrogenation velocity of ethylene on copper at 0°C. to as low as 10 per cent of the normal value. Taylor calculated from these values that the adsorption heat on a surface covered with poison is greater by 1230 calories than at the next active part of the surface.

Garner and Blench,<sup>26</sup> studying the heat of adsorption for oxygen on activated carbon, believed they had direct evidence for the existence of

strongly unsaturated surface atoms with a high energy content of some atoms. On the other hand, there are some investigators who believe increased adsorption ability on active places is greatly overemphasized.

Sauter<sup>79</sup> states that adsorption heats on unsaturated places are only slightly larger than on other parts of the surface. According to Sauter, the increased polarization produced by active centers upon molecules to be activated is one reason for their high reaction ability.

Garner and Kingman<sup>27</sup> believe that both heats of adsorption and energy of polarization would be expected to be greatest when adsorption occurs on the most active parts of the surface. However, Taylor and Kistiakowsky, comparing the activity of single and mixed catalysts, found no evidence for adsorbed molecules being more strongly polarized on mixed catalysts ( $\text{ZnO} + \text{Cr}_2\text{O}_3$ ) than on zinc oxide alone. Garner and Kingman assume that molecules of the adsorbed gas are either dissociated or highly polarized and therefore contain a higher internal energy in comparison with that of the average molecule in a gaseous state. The energy of polarization contributing to the activation of adsorbed molecules is one part of the total energy of the surface atom, the other part being set free as heat. Taylor and Kistiakowsky found that mixed catalysts adsorb hydrogen more readily than carbon monoxide and that chromic oxide adsorbs very little hydrogen and much more carbon monoxide than mixed catalysts.

Garner and Kingman investigated the heats of adsorption and adsorptive capacity of hydrogen and carbon monoxide on zinc oxide, chromic oxide and their mixtures, using a vacuum calorimeter, and found that their heats of adsorption ranged from 25 to 10 Calories per gram-mol. The adsorptive capacity was found to be much greater for mixed catalysts but the heat of adsorption was the same for all three cases. From this they concluded that the greater efficiency of mixed catalysts is due to an enlargement of the internal area of the catalyst.

Table 9. Heats of Adsorption (Kg. Calories/Gram-Mol.).  
(Garner and Kingman)

Catalyst	Hydrogen	Carbon Monoxide
ZnO	..	22 → 18
$\text{Cr}_2\text{O}_3$	..	8 → 11
$\text{ZnO} + \text{Cr}_2\text{O}_3$	20 → 10	24 → 14

In adsorption of gases on the surface of solids, the forces which bind molecules adsorbed from a gas are different only in the fact that the adsorbed molecules are not identical with the particles in the solid. In the adsorption of gases on solids the following possibilities have to be considered:

- (1) Van der Waals' adsorption
- (2) Adsorption due to polar forces
- (3) Activated adsorption
  - (a) reversible
  - (b) irreversible or chemisorption

In the case of van der Waals' adsorption, Eucken ("Lehrbuch der Chem. Physic.," 1930) considers that

$$Q_a = \text{const. } \sqrt{T_b}$$

where  $Q_a$  is the heat of adsorption and  $T_b$  is the boiling point of the specific gas in the liquid state. The extent to which this relation is valid is illustrated in Table 10.

Table 10. Heat of Adsorption of Gases on Wood Charcoal.

Gas	Heat of Adsorption	$T_b$	$(Q_a/\sqrt{T_b})$
H <sub>2</sub>	2500	20.4	550
N <sub>2</sub>	4400	77.3	505
A	4200	87.2	450
CO	4800	83.1	530
CH <sub>4</sub>	5500	111.7	520
CO <sub>2</sub>	7500	194.6	540
NH <sub>3</sub>	8700	240.0	560

Thus the heat of adsorption is approximately proportional to the square root of the boiling point, while according to Trouton's rule, the heat of vaporization of the liquid is proportional to the first power. From this it might seem that a separation of materials which depends on van der Waals' adsorption should be much less effective than a distillation, but exactly the opposite of this is true. In adsorption in dilute films, the mutual effect of the molecules of the adsorbed substance is small. Presumably, however, the principal effect is due to the selection of the most active spots on the surface by that component of the gas which gives the highest heat of adsorption, and which tends to remain at pressures at which the other materials may be pumped off. Also such films are in general mobile, so the molecules diffuse on the surface from spots where they are weakly bound to those whose binding is stronger. If the concentration of the adsorbed molecules becomes too high, then the sharpness of the separation on desorption is greatly lessened. (Harkins.) Such a smallness of separation is particularly useful when the boiling points are almost the same, but the molecules are adsorbed to very different extents. Thus ethane (B. P. — 88.5°C.) and carbon dioxide (B. P. — 79°C.) or hydrogen chloride (B. P. — 85°C.) are readily separated on account of the differences of their polar properties.

An interesting method for the determination of the heat of adsorption on a metal has been developed by J. R. Roberts.<sup>77a</sup> The low pressure is measured by a Pirani gauge, and the rise in temperature of the filament, of the order of 0.01°C., by its use in a sensitive Wheatstone bridge. The filament used had an apparent area of 0.55 sq. cm. For the 110 plane, usually assumed to be the important one, the number of tungsten atoms is  $P \times 14.2 \times 10^{14}$ , and for the 100 plane  $P \times 5.5 \times 10^{14}$ , where  $P$  is the roughness factor, found to be 1.1. The total number of hydrogen molecules adsorbed was found to be 4.3, 3.3, and  $3.8 \times 10^{14}$  in three separate experiments, or of the order of one atom of hydrogen to one of tungsten. Until the film was complete practically all of the hydrogen was adsorbed, that is, the pressure remained below the minimum registered by the

gauge. The heat of adsorption decreased from about 40 kg. cal. per mole at a surface concentration of  $1 \times 10^{14}$  to 20 kg. cal. at  $4 \times 10^{14}$  molecules per square cm. The relation between the heat of adsorption and the amount adsorbed was found to be approximately linear. As has already been pointed out, the evidence indicates that one atom of hydrogen is adsorbed on each tungsten atom in the surface. If this is considered as a 110 plane the atoms are in a rectangular mesh, with elementary rectangles of sides  $a_1$  and  $a/\sqrt{2}$ , with another atom at the center, so that each atom is surrounded by four others at a distance  $a\sqrt{3}/2$ . Roberts considers the heat of removal of a single hydrogen to be  $Q$ ,  $Q - 4x_1$ , or  $Q - 4x_1 - x_2$ , respectively for the bare surface, for four atoms adjacent to the atom removed and for the whole surface covered. The heat of adsorption of  $H_2$  in an immobile film is calculated as follows:

- (1) On a bare surface:
  - (a) Dissociate  $H_2$  into atoms.  
Heat evolved =  $-D$  calories per mol.
  - (b) Adsorb atom 1 on the surface.  
Heat evolved =  $Q$  calories per gram-atom.
  - (c) Adsorb atom 2 on surface next to atom 1.  
Heat evolved =  $Q_1 - x_1$  calories per gram-atom.  
Total heat evolved =  $2Q - D_1 - x_1 = 45,000$  calories per mol  $H_2$  from the experiments at very low pressure (Equation 1).
- (2) On a surface completely covered otherwise:
  - (a) Dissociate the molecule into atoms.  
Heat evolved =  $-D$  calories per mol  $H_2$
  - (b) Adsorb atom 1 on the surface.  
Heat evolved =  $Q - 3x_1 - x_2$
  - (c) Adsorb atom 2 on the surface.  
Heat evolved =  $Q - 4x_1 - x_2$   
Total heat evolved =  $2Q - D - 7x_1 - 2x_2 = 18,000$  calories per mol  $H_2$  (Equation 2).
- (3) Average heat for two neighboring spaces if  $Q$  is the fracture of the surface which is already covered.  
Total heat evolved =  $2Q - D - 2Q(3x_1 - x_2) - x_1$  calories per mol  $H_2$  (Equation 3).

From equations 1 and 2 is derived

$$3x_1 + x_2 = 13,500 \text{ calories.} \quad (\text{Equation 4})$$

In order to determine the relative magnitudes of  $x_1$  and  $x_2$ , it is assumed that the forces between the adsorbed molecules are electrostatic of a magnitude  $\mu^2/2r^3$  ergs, or one-half that between dipoles of dipole moment  $\mu$  (e.s.u.).  $x_1$  ergs are assumed to be the contribution of each adjacent atom to the potential energy where

$$x_1 = (x_1/N_0)4.18 \times 10^7 \quad (\text{Equation 5})$$

and  $x_2$  ergs are assumed to be the contribution of all the other atoms to the potential energy. To calculate the total potential energy, a circle of

radius  $3.2a$  was drawn around the specified atom, and the contribution of each atom in this circle was calculated individually, while that of the outside atoms was calculated by integration on the assumption of a uniform distribution of surface density  $\delta = \sqrt{2}/a^2$  per unit area. Thus three-quarters of the total value of  $x_2$  was calculated directly and only the remainder by integration. This gave

$$\begin{aligned} x_1 &= 0.77\mu^2/a^3 \\ x_2 &= 5.12\mu^2/a^3 \end{aligned} \quad (\text{Equation 6})$$

The change of work function on adsorption is

$$2\pi\mu\delta \text{ (e.s.u.)} \quad (\text{Equation 7})$$

Experimental evidence,<sup>49a, 86</sup> shows that for caesium films on tungsten, the electric moment per atom diminishes as the surface becomes more covered, and this is explained as due to the depolarizing effect on a given adsorbed atom, of the field of the others. The contact potential of the film covered against the bare tungsten is found to be represented by  $V_e/\theta = \text{const. } \mu$ , whereas for thorium on tungsten  $V_e/\theta = 9.8$  for  $\theta = 0$  and  $V_e/\theta = 2.6$  for  $\theta = 1$ , which indicates an effect of a considerable magnitude on the value of  $\mu$ . Roberts finds that the corresponding effect with a film of hydrogen atoms is very small, that is,  $\mu$  is practically constant.

From equation 2,  $Q - 4x_1 - x_2 = (D + 18)/2 - x_2/2$ .

This gives the heat necessary to remove a hydrogen atom from a completely covered surface. From equations 5, 6, and 4,  $x_1 = 1400$  calories. If  $D$  is taken as 101 kilocalories per mol of  $H_2$  and  $\alpha$  as  $3.1 \times 10^{-8}$  cm., the values in the following table are obtained:

Heat of Removal and Dipole Moment of Hydrogen Atoms on a Tungsten and a Caesium Surface.

Heat in Kilocalories per mol to Remove Atom		Dipole Moment per Adsorbed Atom (e.s.u.)	Change in Work Function in Volts
First	Last		
58.8	73.7	$1.94 \times 10^{-18}$	5.2
For a caesium surface		$3.9 \times 10^{-18}$	

The sign of the dipole is the same for films of hydrogen and oxygen, but opposite for caesium.

The heats of adsorption, determined by direct measurement for a number of gas-metal systems at ordinary temperatures, are given in Table 11.

Tables 12, 13, and 14 present values obtained by different observers for heats of adsorption for hydrogen, oxygen, and carbon monoxide, respectively.

According to Sauter,<sup>79</sup> it is more reasonable to consider that unsaturated places are places where reactions occur more often. This idea advocated by Taylor does not find support in calculations made by Herzfeld<sup>33</sup> in which he considered a dipole adsorption as that adsorption occurring on both positive metal ions in the lattice and the electrons between causing an attraction between adsorbed molecules. An increase in the heat of adsorption is attributed to these additional attractive forces. Herzfeld

Table 11. Heats of Adsorption for Gas-Metal Systems.

Metal	Gas	Temp. (°C.)	Heats of Adsorption (Calories/g. mol.)	Observer
Cu	H <sub>2</sub>	25	9,000- 14,000	Ward: <i>Proc. Roy. Soc. London (A)</i> , <b>133</b> , 506 (1931).
			4,000- 16,000	Taylor, Kistiakowsky and Perry: <i>J. Phys. Chem.</i> , <b>34</b> , 799 (1930).
			11,500- 17,500	Taylor, Kistiakowsky and Perry: <i>J. Am. Chem. Soc.</i> , <b>49</b> , 2200 (1927).
			11,500- 13,500	Beebe: <i>Trans. Faraday Soc.</i> , <b>28</b> , 761 (1932).
Cu	CO	0	9,000- 30,000	Beebe: <i>Ibid.</i> , <b>28</b> , 761 (1932).
			13,000- 20,000	Benton and White: <i>J. Am. Chem. Soc.</i> , <b>54</b> , 1373 (1932).
			13,500- 20,300	Beebe and Wildner: <i>Ibid.</i> , <b>56</b> , 642 (1934).
Ni	H <sub>2</sub>	0	14,000	Taylor: "Physical Chemistry," 2nd Ed., Vol. II.
			10,000- 30,000	Fryling: <i>J. Phys. Chem.</i> , <b>30</b> , 818 (1926).
			12,500	Rideal: <i>J. Chem. Soc.</i> , <b>121</b> , 309 (1922).
Ni	O <sub>2</sub>	0	100,000	Taylor: "Physical Chemistry," 2nd Ed., Vol. II.
Pt	H <sub>2</sub>	20	14,000- 17,200	Maxted and Hassid: <i>J. Chem. Soc.</i> , <b>1931</b> , 3313.
		0	10,000- 30,000	Taylor and Kistiakowsky: <i>Z. physik. Chem.</i> , <b>125</b> , 341 (1927).
	O <sub>2</sub>	0	33,000-161,000	Taylor and Kistiakowsky: <i>Ibid.</i> , <b>125</b> , 341 (1927).
	CO	0	18,000- 35,000	Taylor and Kistiakowsky: <i>Ibid.</i> , <b>125</b> , 341 (1927).
	SO <sub>2</sub>	0	15,000- 37,000	Taylor and Kistiakowsky: <i>Ibid.</i> , <b>125</b> , 341 (1927).
Ag	O <sub>2</sub>	100	12,000- 15,000	Benton and Drake: <i>J. Am. Chem. Soc.</i> , <b>54</b> , 2186 (1932).
		197	15,000- 23,000	Benton and Drake: <i>Ibid.</i> , <b>56</b> , 255 (1934).
W	H <sub>2</sub>		18,000- 28,000	Roberts: <i>Proc. Roy. Soc. London (A)</i> , <b>152</b> , 445 (1935).
			320,000	Blodgett and Langmuir: <i>Phys. Rev.</i> , <b>40</b> , 78 (1932).
			139,000	Roberts: <i>Proc. Roy. Soc. London (A)</i> , <b>152</b> , 464 (1935).
Pd	CO	0-184	7,000- 15,000	Taylor and McKinney: <i>J. Am. Chem. Soc.</i> , <b>53</b> , 3604 (1931).
Fe	H <sub>2</sub>	-96 to -78	10,400 ± 1,000	Emmett and Harkness: <i>Ibid.</i> , <b>57</b> , 1631 (1935).

calculated the contributions of translational, vibrational, and rotational energy of a free molecule made to a change in the heat of adsorption when the molecule is bound to the surface and found that conversion of the translational energy into energy of oscillation could cause a change of 80 calories per degree of freedom. The rotational energy could change the heat of adsorption of about 2,100 calories, thereby converting all degrees of freedom into degrees of oscillation. To fulfill this requirement, the molecule would have to adhere to more than one active spot on the surface. Balandin's multiplet theory emphasizes not so much the nature of the points of attraction on the surface as their interrelationship and the

Table 12. Heats of Adsorption for Hydrogen.

Adsorbent	Activation Temperature	Adsorption Heat	Observer
Pd black	Decrease in adsorption with increase in temperature from liquid air temperature, and upward; minimum adsorption occurs at about 20°; previous saturation at 110° always gave higher values; high solubility of the gas in the metal complicated conditions with palladium.		Firth: <i>J. Chem. Soc.</i> , <b>119</b> , 1120 (1921). Guthier, Gebhard and Ottenstein: <i>Ber.</i> , <b>46</b> , 1453 (1913).
Pd	Higher adsorption of hydrogen at -78° than at 0°.	No data for heats of adsorption.	
Pd foil massive	No adsorption of hydrogen at liquid air temperature.		Firth: <i>J. Chem. Soc.</i> , <b>117</b> , 171 (1920).
Ni	Low adsorption at -190°, high adsorption at -100°, -209°, and -305°.	At 0°, 15,000 cal.	Benton and White: <i>J. Am. Chem. Soc.</i> , <b>52</b> , 2325 (1930). Gauger and Taylor: <i>J. Am. Chem. Soc.</i> , <b>45</b> , 920 (1923).
Cu	Pronounced maximum in adsorption of hydrogen from 0-100°; at 100° and 155°, adsorption slightly greater than at 0° but less than at 193°.	Pronounced maximum in the curve for the heat of adsorption of hydrogen on active copper catalyst	Harris: University of Virginia, 1924. Taylor and Kistiakowsky: <i>Z. phys. Chem.</i> , <b>125</b> , 341 (1927).
C Charcoal	At -78° and at liquid air temperature, adsorption greater than at 0° and greatest at the lowest temperature.	Activation energy must be small; no data for heats of adsorption.	Dewar: <i>Proc. Roy. Inst.</i> , <b>18</b> , 437 (1906). Bonhoeffer and Harteck: <i>Z. phys. Chem.</i> , <b>4B</b> , 113 (1929).
Cu		Indicate an activation energy for hydrogen adsorption although the heat of adsorption was only 10,000 calories for hydrogen as compared with 15,000 cal. for ethylene; experiment shows that adsorbed ethylene is removed more readily than hydrogen.	Washburn: Unpublished data. Taylor, Kistiakowsky and Perry: <i>Z. phys. Chem.</i> , <b>34</b> , 799 (1930).
Pt	Decreased adsorption at -78°.	At 0°, 10,000 to 30,000 cal.	Taylor, Kistiakowsky and Perry: <i>Z. phys. Chem.</i> , <b>34</b> , 799 (1930). deHemptinne: <i>Z. phys. Chem.</i> , <b>27</b> , 429 (1898).

activation by adsorption on the exposed atoms of the surface which Taylor assumed would require a juxtaposition of at least two such points to bring about activation and as much activity as on the exposed atoms would be expected than in between two surfaces.

### Heat of Dissociation

The heat of dissociation has been determined from calculations on the thermal losses of the gas. Kunsman,<sup>45</sup> as well as Lamar and Deming,<sup>46</sup> used this method to determine the heat of dissociation for ammonia on heated filament catalysts. The heat losses were determined by the equation  $W = S(\Phi_2 - \Phi_1) + qK\theta$ , where  $W$  represents thermal losses;  $S$ , the constant known as "shape factor," and  $\Phi_2 - \Phi_1$ , the loss by radiation.

$$\Phi_2 - \Phi_1 = \int_{T_1}^{T_2} K \cdot dt$$

where  $K$  is the thermal conductivity of the gas at temperature  $t$ , and

Table 13. Heats of Adsorption for Oxygen.

Adsorbent	Activation Temperature	Adsorption Heat	Observer
Pt		Approximately equal to heat of formation of platinum oxide (ous).	Mond, Ramsay and Shields. <i>Phil. Trans. (A)</i> , <b>186</b> , 661 (1895); <b>190</b> , 129 (1897).
W	Stability of the oxide film on tungsten is so great that no interaction with hydrogen takes place up to 1500°.	160,000 cal. per gram-atom.	*Langmuir: Lecture at Princeton University, September, 1929; <i>Phys. Rev.</i> , <b>24</b> , 570 (1924).
Charcoal	At -185°.	3,744 cal. per mol.	Dewar: <i>Proc. Roy. Soc., London (A)</i> , <b>74</b> , 126 (1904); <i>Proc. Roy. Inst.</i> , <b>18</b> , 184 (1905).
	At 0°.	72,000 cal. per mol.	Garner: <i>J. Chem. Soc.</i> , <b>125</b> , 1288 (1924); <b>130</b> , 2451 (1927). McKie: <i>J. Chem. Soc.</i> , <b>1928</b> , 2870. Cameron: <i>Trans. Far. Soc.</i> , <b>26</b> , 239 (1930).
		89,000 cal. at nearly zero conc. to 70,000 cal.	Keyes and Marshall: <i>J. Am. Chem. Soc.</i> , <b>49</b> , 156 (1927).
		227,000 cal.	Blench and Garner: <i>J. Chem. Soc.</i> , <b>125</b> , 1288 (1924).
			†Taylor (G. B.), Kistiakowsky and Perry: <i>J. phys. Chem.</i> , <b>34</b> , 799 (1930).
Pt	Adsorption fairly rapid at 0°; no data for lower temperatures.	163,000 cal. per mol of oxygen adsorbed; 100,000 cal. usual value.	†Taylor (G. B.), Kistiakowsky and Perry: <i>J. phys. Chem.</i> , <b>34</b> , 799 (1930).
Pt Fe <sub>2</sub> O <sub>3</sub> Cr <sub>2</sub> O <sub>3</sub>		2,200 to 700 cal. per mol calculated from isothermals; considerably higher values were obtained by direct measurement.	Neuman and Goebel: <i>Z. Elektr.</i> , <b>40</b> , 754-764 (1934).

\* Langmuir found a change in the state of oxygen adsorption between liquid air temperature and room temperature.

† Taylor explains the unusual increase in the heat data from liquid air temperature to room temperature by the multiplicity of processes in the fixation of oxygen by charcoal.

Table 14. Heats of Adsorption for Carbon Monoxide.

Adsorbent	Activation Temperature	Adsorption Heat	Observer
Ni	At 180°, the reaction between CO and Ni to form Ni(CO) <sub>4</sub> is suppressed; at 270°, CO is irreversibly adsorbed; the actual activation process related to the formation of Ni <sub>4</sub> C and NiO occurs at 270°.		Taylor and Burns: <i>J. Am. Chem. Soc.</i> , <b>43</b> , 1283 (1921). Bahr and Bahr: <i>Ber.</i> , <b>61B</b> , 2177-2465 (1928).
Cu	The activation energy of this adsorption is very high; no evidence as to adsorption increasing over a temperature range has been obtained.	10,000-20,000 cal.	Taylor and Kistiakowsky: <i>Z. phys. Chem.</i> , <b>125</b> , 341 (1927).
Pt	Adsorption of CO on Pt less at -78° than at +15°; smaller values at 25° than at 110°; reversibility of CO adsorption on Pt is slight; the activation energy of the adsorption process higher for CO than hydrogen.	Heat of adsorption greater than 20,000 cal.	deHemptinne: <i>Z. physik. Chem.</i> , <b>27</b> , 429 (1898). Taylor and Burns: <i>J. Am. Chem. Soc.</i> , <b>43</b> , 1283 (1921). Langmuir: <i>J. Am. Chem. Soc.</i> , <b>40</b> , 1361 (1918).
Pd	No change between 25° and 110°; increase of CO adsorption between -78° and +15°.		Taylor and Burns: <i>Ibid.</i> , <b>43</b> , 1283 (1921). deHemptinne: <i>Z. physik. Chem.</i> , <b>27</b> , 429 (1898).

$T_1$  and  $T_2$ , the temperatures of the water bath and of the surface of the metal.

The average heat of dissociation of ammonia for temperatures between



954° and 1164°F. was found to be 12,067 calories per mol. Lewis and Randall<sup>62</sup> obtained for  $q$ , a value of 13,375 calories per mol for the same temperature range, by using a formula based on Haber's data.

### Heat of Evaporation = Heat of Adsorption

The heat of evaporation of adsorbed hydrogen from the nickel surface was calculated from the Clapeyron equation,  $\frac{d \ln P}{dT} = \frac{\lambda}{RT^2}$ , where  $P$  is the saturation pressure in mm. mercury;  $T$ , the absolute temperature;  $\lambda$ , the heat of evaporation per gram-molecule, and  $R$  is equal to 1.99. Integrating and passing to Briggs' logarithms:  $\lambda = 1.99 \times 2.303 \frac{T_1 \cdot T_2}{T_2 - T_1} \log \frac{P_2}{P_1}$ .

Table 15. Heat of Adsorption = Heat of Evaporation.

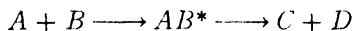
Adsorbent	Gas	Calories	Observer
N <sub>2</sub>	H <sub>2</sub>	2,500 (determined from the variation in saturation pressure with temperature).	Gauger and Taylor: <i>J. Am. Chem. Soc.</i> , <b>45</b> , 920 (1923).
Ni	H <sub>2</sub>	12,000 (calculated by assuming that the rate of reaction in the presence of traces of oxygen is proportional to the rate of evaporation of hydrogen from the surface, the velocity of which was plotted against the reciprocal of absolute temperature, obtaining a straight line; from the slope of this curve the value of 12,000 was obtained).	Rideal: <i>J. Chem. Soc.</i> , <b>121</b> , 309 (1922).

### Activated Adsorption or Chemisorption

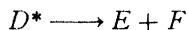
It has long been recognized that gaseous substances may react with the surface of a solid to give an adsorption that is chemical in nature. Thus Calvert<sup>8a</sup> found that the oxygen adsorbed on charcoal between 0° and 150°C. is not readily recoverable, but oxidizes ethylene to carbon dioxide and water, and ethyl alcohol to acetic acid. Smith<sup>82a</sup> and many others have found that at still higher temperatures, very little uncombined oxygen can be recovered, but what is removed consists of carbon monoxide and carbon dioxide. For the low temperature type, Dewar<sup>11a</sup> found the heat of adsorption at liquid air temperatures to be 3,750 calories per mol, while at 0° Keyes and Marshall<sup>39</sup> obtained a value of 72,000 calories for the first gas adsorbed.

It has been known for a long time that many chemical reactions will not occur without the addition of an energy of activation, which is often assumed, as in the theory of Eyring and Polanyi<sup>18b</sup> to be the energy necessary to raise the system to the top of a potential barrier before the reaction can take place. This idea is often presented as indicating the formation of an activated complex, or intermediate temporary chemical compound, which commonly has a life of the order of  $10^{-13}$  second. In the case of adsorption, this activated complex, a compound formed between the gaseous particle and the solid, may change into a stable form by loss of energy, or it may react with another activated complex to form another compound or compounds which may then be desorbed. This type of reaction which is brought about by activated adsorption on a surface has been designated as heterogeneous catalysis (Harkins). The recognition that an activated intermediate complex plays the major role

in nuclear reactions occurred since Harkins and Shadduck<sup>31a</sup> considered that all nuclear reactions occur as follows:



If  $D$  is still activated, then



Here the life of the intermediate nuclear compound is of the order of  $10^{-22}$  to  $10^{-13}$  second, and often about  $10^{-18}$  to  $10^{-16}$  second. The energy of activation of the nuclear compound is of the order of a million times that of the chemical complex. The origin of the energy  $E$  of activation of the nuclear excited compound is very simple, since it includes (1) the kinetic energy of  $A$  and  $B$  minus the kinetic energy of  $AB^*$ , and (2) the sum of the masses of  $A$  and  $B$  minus the mass of the stable form of  $AB$ . Thus:

$$E = E_A' + E_B' - E_{AB^*}' + 9 \times 10^{20}(m_A + m_B - m_{AB}) \quad (1)$$

where  $9 \times 10^{20}$  is the square of the velocity of light ( $c^2$ ), and indicates that the energy is kinetic. In the disintegration of  $AB^*$  into  $C$  and  $D$ , the activation energy  $E$  is transformed partly into their kinetic energy and partly into the increase of mass above the mass of the stable  $AB$ , or

$$9 \times 10^{20}(m_C + m_D - m_{AB}) + E_C' + E_D' = E_{AB^*}' + E \quad (2)$$

It is obvious, says Harkins, that if the activated intermediate nuclear compound is to be formed, the nuclei  $A$  and  $B$  must have sufficient energy to supply both the energy of activation and the kinetic energy  $AB^*$ . The relations of chemical reactions are similar, but since the changes of mass are very minute, it is not convenient to treat the energy of activation of the intermediate complex in terms of mass relations. The energy of activation is determined by the energy barrier over which the system must pass before the reaction can occur.

In Fig. 1,  $E$  represents the energy of activation and  $\lambda$  the heat of reaction. The latter quantity may be determined directly by calorimetric measurements or from the change in gas pressure of the gas with temperature by the application of the equation of Clapeyron. The energy of activation is determined from the change of the velocity of the reaction between the solid and the gas adsorbed, by the use of the equation of Arrhenius. For example Taylor and Williamson<sup>88b</sup> calculated the activation energy of hydrogen on a manganese oxide-chromium catalyst by this equation in the form

$$E = \frac{4.58(\log V_1 - \log V_2)}{\frac{1}{T_2} - \frac{1}{T_1}}$$

from the velocities  $V_1$  and  $V_2$  at temperatures  $100^\circ$  and  $132^\circ\text{C}$ . on what they considered to be a clean surface.

The relations for the activated adsorption of hydrogen or oxygen on

a metal have been presented in the form of potential curves by Lennard Jones<sup>38a</sup> (Fig. 2):

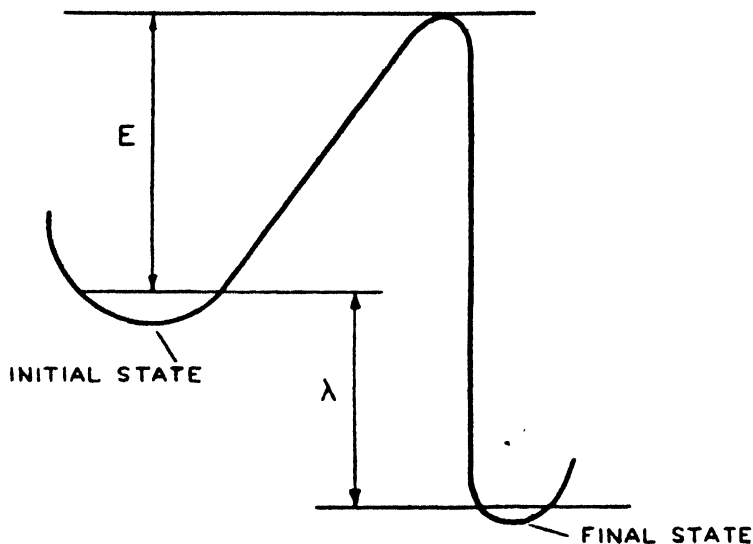


FIGURE 1.

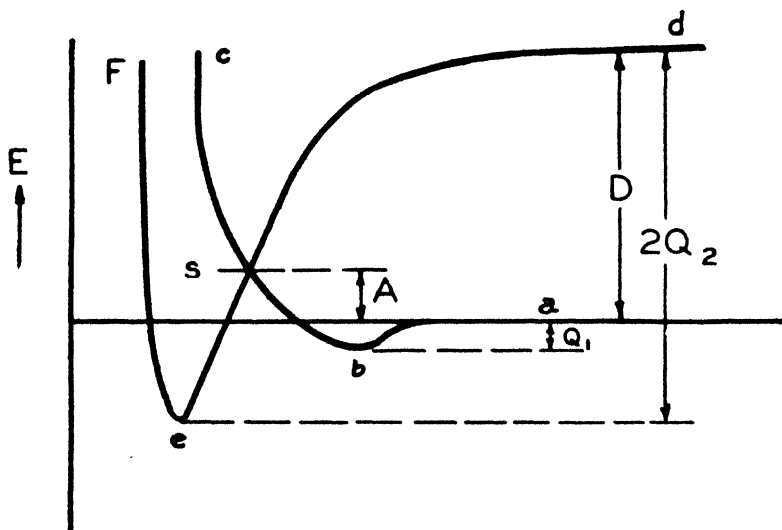


FIGURE 2.

The curve  $abc$  represents the energy content of the system. Metal +  $H_2$  as the molecule approaches the surface. The minimum  $b$  is the equilibrium position and  $Q$ , the energy of adsorption. If the gaseous hydrogen molecules are to be dissociated into atoms, the energy of dissociation  $D$  (from

*a* to *d*) must be added. The atoms can now be strongly adsorbed on the surface to form surface hydride molecules. The energy of formation  $Q_2$  can be so great that  $2Q_2 > D + Q_1$ . The potential curve for this reaction *def* cuts *abc* at *S*, which is an amount of energy *A* above the level *a*. Hydrogen molecules do not then need to be first dissociated into atoms to be adsorbed. It is sufficient that the kinetic energy of the molecules striking the surface be greater than *A*. The molecules have thus the energy necessary to reach the point *S*, since their energy *W* is greater than *A*, and the molecules reach the distance from the surface corresponding to *S* where no energy is needed for the dissociation of the molecules. By the action of the potential energy due to the atoms of the surface, the atoms are drawn closer to the surface to the position *e*.

### Heats of Activation

Molecules react when their internal energy is raised to a certain critical value. This "critical energy," in the terms of Marcelin, measures to a certain extent the solidity of the bond uniting various parts of the molecule structure. This viewpoint of Marcelin and Rice<sup>67</sup> and that of Trautz and Krüger,<sup>92</sup> considering the source of energy making chemical reactivity possible, the infrared radiation, constituted the hypothesis of the "critical energy" increment advocated by Lewis.<sup>51</sup> On the other hand, to bring about a chemical reaction a certain energy of "activation" is required. According to Palmer<sup>55</sup> the term "activation" implies not only the adsorption of energy necessary for a reaction to take place, but also the adsorption of a radiation from atoms of the catalyst. This theory emphasizes not only the fact that the specific action of a catalyst lies in selective adsorption, but that it requires radiation of the proper quality. It is apparent that the conceptions of critical energy and activation have the same characteristics.

It is a well-known fact that only a few of the collisions between reacting molecules result in a reaction, and that to make the collisions effective, the energy of activation is necessary. Lewis<sup>51</sup> considered the fact that the sum of the critical energy increments necessary to activate the reactants at the surface of a catalytic substance and the energy required to desorb the products of the reaction is less than that required to activate the reactants in the free state. Therefore, the critical energy increment for activation of hydrogen and oxygen at the surface must be less than that necessary for activation of hydrogen and oxygen in the free state. If the activation energy is very small, the substances are unsaturated; with an increase in activation, the activating substances become more saturated. This conception of saturation has a quantitative basis obtained through values of activation heats.

Since the collision of molecules determines the activation energy, space conditions or the steric factor are significant.

Eyring<sup>18a</sup> and Sherman and Eyring<sup>82</sup> ascertained that in the case of large atomic distances in the solid body the activation energy is high. On the other hand, surface atoms with most favorable distances are those

occupied during activated adsorption, *i.e.*, the magnitude of the activation energy is determined by the deviation of two atomic distances from the most favorable one. On the basis of these conceptions, a relationship has been deduced between favorable positions (active centers) of the catalyst and the activation energy of adsorption and desorption according to which the distance of minimum activation energy determines the most active centers. Of course, it should not be overlooked that favorable spacing may also be a function of the chemical nature of surface atoms.

Sherman and Eyring<sup>82</sup> calculated the energy for various carbon-carbon distances and for various positions of approaching molecules, and deduced that the "easiest energy path" is from the state of molecular hydrogen to that in which each hydrogen is attached to one of the carbon atoms. They found that the activation energy required was very sensitive with respect to the carbon-carbon distance in the solid body. On account of the repulsive forces operating between the four atoms with small atomic distances in the solid, the activation energy is high. Even with large atomic distances in the solid the activation energy is high, since the process involves complete separation of the atoms of the hydrogen molecule. At some intermediate distance in the solid, the activation energy passes through a minimum. From this reasoning Sherman and Eyring postulated that it is this distance, corresponding to a minimum activation energy, which determines the most active centers, and that variations in atomic distances are associated with variations in the activation energy.

The heats of activation for all types of chemical conversions may be calculated through data obtained on mutual atom positions or atomic distance and the forces acting between them. Atomic positions are estimated from stereo-chemical conceptions, while atomic distances, or atomic forces (partial electric forces), obey Coulomb's law.<sup>2</sup>

The statement that the activation heat is less than the sum of the heat of decomposition into atoms is true for every conversion. Therefore the existence of an upper limit for all activation heats is assumed to be:

$$\begin{array}{r}
 -4,540 \text{ cal. (Bodenstein)} \\
 -(\alpha Q_{H_2} + \beta Q_{I_2}) + 28Q_{HI} = -2,900 \text{ cal. (Stegmüller)} \\
 \text{(Heat of Formation of HI)}
 \end{array}$$

The kinetic measurements gave:

$$\begin{array}{l}
 \alpha Q_{H_2} + \beta Q_{I_2} = 39,500 \text{ cal.}; 2\gamma Q_{HI} = 44,040 \text{ cal.} \\
 Q_{H_2} = Q_{I_2} = 118,000 \text{ cal.}; \alpha = \beta = 0.299; \gamma = 0.261 \\
 2Q_{HI} = 115,100 \text{ cal.}
 \end{array}$$

Trautz<sup>91</sup> estimated that, for the conversion into the active state, the atoms must be so separated that one-third to one-fourth of the decomposition energy can be introduced. Trautz considered it possible to deduce how far atoms can be separated from the knowledge of the position and forces in the atomic group, but to solve the problem whether the active intermediate state corresponds to a definite intermediate product has been rather difficult. Trautz established a rule according to which all reaction

velocity constants have the same formula:  $K = Se^{\frac{-W}{RT}}$ , where  $K$  is the specific reaction rate constant;  $S$ , the proportionality factor equal to the number of collisions per unit concentration of the colliding substance, and  $W$ , the activation heat of the reaction.

According to Taylor,<sup>86a</sup> the heat of activation may be calculated from temperature coefficients by the equation:  $d\ln K/dT = E/RT^2$ . Steacie<sup>82b</sup> opposed Taylor's viewpoint that adsorption in many cases does not occur instantaneously and is a slow process which requires an energy of activation in catalysis by stating that it is rather the solubility of gases (in metals) that is involved.

Activated adsorption is specific and is not governed, as is van der Waals' adsorption, principally by extension of surface. The heats of activated adsorption of hydrogen as ascertained are about one order higher than those of van der Waals' adsorption. This difference in the heats involved is decisive in differentiating the ordinary classical adsorption (van der Waals') from the other process (H. S. Taylor's). Activated adsorption is regarded as a true surface process proceeding at a slow rate, and not due to penetration into deeper parts of the mass than are accessible to rapid van der Waals' adsorption. Howard<sup>37a</sup> has shown that van der Waals' and high-temperature adsorptions are not additive. The latter modifies the former. The rapid van der Waals' adsorption is not affected by previously activated adsorption of hydrogen in the sense of the speed with which equilibrium is attained.

Taylor and Williamson<sup>88b</sup> showed that promotion of manganous oxide by chromium oxide materially lowers the activation energy of the first hydrogen adsorbed. The activation energy was found to increase with increasing extent of surface covered and this was considered proof for non-uniform surface activity.<sup>88a</sup>

Polanyi<sup>72</sup> attributed the difference in the activation heats of catalyzed and non-catalyzed reactions to the fact that instead of a process of dissociation the process of decomposition of an intermediate compound takes place. Sauter<sup>79</sup> illustrates this viewpoint by the hydrogenation of ethylene on nickel catalyst, stating that in the chemical sorption of hydrogen molecules the hydrogen atoms are separated from one another by only short distances. Since no splitting of the hydrogen molecules takes place, chemical sorption corresponds to closing of one bond. This is set loose in catalysis with the closing of the ethane bond and this requires only a small activation heat.

Langmuir<sup>48</sup> pointed out that the essential difference between catalyzed and non-catalyzed reactions from an energetic point of view is due to the fact that collisions between gaseous molecules and a solid differ from ordinary kinetic collisions in a homogeneous gas phase in being comparatively inelastic. The colliding gas molecule remains on the catalyst surface for an interval of time which is long in comparison to that in ordinary gaseous collisions; therefore a greater opportunity is given for activation to occur.

Porter<sup>75</sup> considered that energy of activation is the energy which makes collisions between reacting molecules effective. The factor is  $e^{-Q/RT}$ , where  $Q$  is the heat of activation for the number of active collisions between reacting molecules and is decreased by one-third of the number of freedom diminished by one unit.

The term "activation" has been interpreted also as the adsorption of energy brought about by the adsorption of a radiation from atoms of the catalyst.<sup>66</sup>

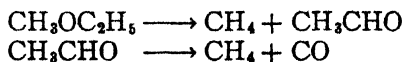
Rideal<sup>77</sup> emphasized also the existence of a "critical increment" of energy necessary for the activation of a reacting substance and considered it not as a unique property of the element, but as one varying with the catalyst used. He deduced physical characteristics for an active catalyst from the hypothesis of Stark and Thomson based on atomic structure.

Palmer applied the quantum theory of radiation to calculate the heat of activation in the reduction of isopropyl alcohol, using copper as a catalyst. The measure of the maximum number of alcohol molecules activated by the catalyst is given by  $A$ , using this equation for the catalytic activity:  $V = Ae^{-K/T}$ . From the quantum theory of radiation it follows that:  $\frac{N h \nu}{K} = R$ , where  $N = 6.06 \times 10^{23}$  (Avogadro's number);  $h = 0.742\mu$ ;  $\nu = 4.04 \times 10^{14}$ , and  $KR$ , the heat of activation of alcohol in calories per gram-molecule, or  $1.98 \times 19.380 = 38.740$  calories.

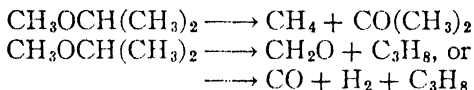
Elöd and Banholzer<sup>17</sup> calculated the heat of activation,  $E$ , of the decomposition of ammonia on copper from the reaction velocity constants, using the equation:  $E = 2.303 \left( \log_{10} \frac{K_2}{K_1} \right) \left( \frac{T_1 \times T_2}{T_2 - T_1} \right)$ , where  $2.303 = R$  and is the gas constant expressed in calories per molecule per degree;  $K_1$  and  $K_2$ , the velocity constants at absolute temperature,  $T_1$  and  $T_2$ . The value of  $\log_{10} K$  corresponds to a certain total flow rate of gas plotted against  $1/T_1$  resulting in a curve the slope of which was used to calculate  $E$ . The most probable value for  $E$  was  $46,000 \pm 2,000$  calories per molecule.

Kunsman<sup>44</sup> investigated the heat of activation for the thermal decomposition of ammonia, using promoted iron as catalyst, and found that, with an eighteen fold variation in the catalytic activity, the values ranged from 38,000 to 42,000 calories. From this Kunsman deduced that the heat of activation is a function of the reacting gas rather than of the catalyst. Hinshelwood and Burk,<sup>35</sup> however, disagreed with Kunsman's conclusion as their measurements on the thermal decomposition of ammonia on tungsten indicated a considerable reduction in the heat of activation.

Clusius,<sup>10</sup> on the other hand, investigating the decomposition of gaseous ethers, obtained evidence to substantiate the fact that the heat of activation is smaller for the more complicated molecules. Methyl-ethylether decomposes catalytically, iodine being used as a catalyst, between 460° and 550°, according to these reactions:



The heat of activation was found to be 38,000 calories. Methyl isopropyl ether undergoes a double decomposition between 450° and 520°:



The heat of activation was found to be 29,500 calories. These results show that the behavior of hydrogen atoms in a radical is very much influenced by the presence of a second radical in a mixed ether. From this Clusius concluded that the heat of activation is a function of the reactant molecule, dependent on the structure of the whole molecule, and not due primarily to the presence of a certain group. As for the differences in activation heats of various ethers in a non-catalyzed decomposition, Clusius found that it increased with the complexity of the molecule (refer to Table 16). However, since there was considerable evidence of catalytic influence, the results obtained for simple ethers do not necessarily apply to other cases.

Table 16. Decomposition of Ethers (Clusius).

Ethers	Catalyzed Calories	Non-catalyzed Calories
Dimethylether.	with iodine, no catalytic effect	65,000
Methylethylether.	38,000	47,000
Diethylether.	34,000	53,000
Methylisopropylether.	29,500	"
Diisopropylether.	28,500	60,500
Acetaldehyde.	32,500	45,500

Adadurow's<sup>1</sup> investigation concerning the heats of activation in catalytic processes showed the incorrectness of the assumption according to which the value of the activation heat is not influenced by the nature of the catalyst but only by the nature of the reactants. He obtained evidence showing that equal activation heats for a definite catalyst are due to equal energy amounts necessary for splitting off a definite radical. Adadurow found in dehydrogenation reactions of cycloparaffins that the heat of activation,  $E$ , is a function of the catalyst and that the dependence of the activation heat upon the nature of the catalyst is caused by an energy amount introduced into the system by the catalyst. This energy amount for a given catalyst was considered by Adadurow as relating to the wave length radiating from the catalyst at a definite temperature. In general,  $\lambda = 28.4/Q$  and is the wave length of light effective for the same reaction. Values calculated for  $\lambda$  were found to be in agreement with those observed by Adadurow for the rare earths and other  $\text{R}_2\text{O}_3$  oxides, and for the metals platinum, nickel, lead, molybdenum, iron and tungsten. It was also noted that adsorption and desorption heats may produce an additional influence on the activation heat, although no direct relationship to the catalytic properties of the catalyst was established.

Balandin and Rubinstein<sup>2a, 2b</sup> attempted to determine the activation heats of parallel reactions with a mixed catalyst  $\text{Ni}:\text{Al}_2\text{O}_3 = 1:1$  for which each component accelerates its own reaction.



Table 17.

(Balandin and Rubinstein)

Type of Reaction	Activation Heat (cals)
Dehydrogenation of isoamyl alcohol.	8,850-22,400
Dehydration of isoamyl alcohol.	17,950-45,100
Decomposition of the formed valeric aldehyde.	14,500-33,100

The quotient from the named activation energies was found to be constant for a great number of experiments and this led to the assumption that all catalytic processes occur at the boundary Ni/Al<sub>2</sub>O<sub>3</sub>.

Finkelstein, Rubanik and Crisman<sup>21</sup> studied the combustion kinetics of carbon monoxide in the presence of various catalysts. In the case of slightly active catalysts, such as chromium oxide, zinc oxide, aluminum oxide, and chamotte, the activation heats lie between 2,500 and 2,600 calories per molecule, while for active catalysts, such as copper oxide, manganese dioxide and pyrolusite, the activation heats were smaller, 800 to 1,000 calories per molecule. From this these investigators deduced that in the first group of catalysts the adsorption heats are almost equal.

Burk,<sup>8</sup> who also believed that the surface factor is essential in the diminution of activation heat in adsorption catalysis, assumed that it is caused by disruption of molecules. He concluded, therefore, that a mixed surface with two types of adsorbed molecules will have a stronger action than an equally large surface of both pure ingredients.

It has been assumed that in a suitable space distribution of both adsorbents one of these adsorbents will act especially on one atom of the adsorbed molecule, while the other adsorbent will act on the second adsorbed molecule. The activation heats obtained for platinum-tungsten alloy surface were 3,400 to 3,600 calories per gram, while pure platinum gave 13,000 calories per gram and pure tungsten 4,700 to 4,800 calories per gram.

Page and Taylor<sup>64</sup> are of the opinion that the activation energy of the adsorption process is related to an arrangement of atoms of the catalyst favoring adsorption.

Meyer and Hüttig<sup>62</sup> introduced the qualitative and quantitative conception of catalytically active places  $n'$  by expressing in an equation the relation between the degree of catalytic activity  $\alpha$  and the activation heat  $q$ ,  $\log \alpha = q(1.986 - 2.3026/T_2) + \log n'$ . These investigators give in tabulated form the values for  $q$  and  $n'$  for a series of temperatures,  $T$ . The activation heat for the decomposition of nitrogen monoxide with a catalyst mixture  $\text{MgO} + \text{Cr}_2\text{O}_3 \longrightarrow \text{MgCr}_2\text{O}_4$ , proceeding through active intermediate states which, at room temperature, has practically an unlimited span of life, was found to be 23,000 calories at room temperature. The first maximum catalytic activity is at 300° to 400° and found to be due to a decrease of  $q$  to about 9,000 calories. A higher preheating (600°) of the substance makes this effect disappear, restoring the initial value of  $q$ . Continued heating to 700° again causes a decrease in  $q$  up to 6,000-1,000 calories, followed by an increase. The changes in the value of  $n'$  proceed similarly to those of  $q$ , the only difference being that the changes

in the  $\log n'$  are comparatively smaller, and the observed activity increases with a decrease in  $q$ .

Schwab<sup>80</sup> states that the surface molecules of a catalyst attain a stable energy distribution at a definite temperature of preparation of the catalyst which he assumes is maintained under cooling. Excess energy of active centers is related to the heat of activation.

Porter<sup>75</sup> pointed out that in catalytic action the heat of activation remains constant. In the case of a catalytic reaction, polar molecules in the gas space, in proximity to the adsorption layer, are so oriented that their poles are in a direction opposite to the poles of the adsorbed molecules entering the gas space. This decreases the factor  $C^{-Q/RT}$  by one-third.

The interrelationship between temperature and the value of activation heat has been emphasized by Dohse<sup>14</sup> in his study of the decomposition of methanol on zinc oxide catalyst. The reaction proceeds in two steps.

Using the equation:  $\log \frac{C}{1/T}$ ,  $C$  being the amount of the end-product obtained per unit of time, it is graphically shown that the velocity constants and the activation heat of both steps of the reaction may be determined. Balandin<sup>2c</sup> expressed the logarithmic relationship between  $K_0$  and  $Q$  in the equation  $K = K_0 C^{\frac{-Q}{RT}}$ , where  $K_0 = aQ + b$ ;  $a = 0.00112$ , and  $b = 0$ .

Regarding the temperature factor in catalytic adsorption processes, Taylor<sup>84, 85</sup> differentiated between adsorption at low temperature and adsorption at high temperature with high binding energies which he designated as "activated" adsorption. From this he concluded that activated adsorption is absent at low temperatures and that the temperatures at which activated adsorption manifests itself is a function of the activation energy characteristic for the solid surface-gas mixture system.

Table 18.

Gas	Surface	Temp.* (°C.)
Hydrogen.	Copper; nickel.	liquid air
Hydrogen.	Zinc oxide; manganese dioxide a mixture of zinc oxide and manganese dioxide with chromic oxide.	0-100
Hydrogen.	Alumina; glass.	400

\* At which activated adsorption appears.

Taylor pointed out the fact that processes of adsorption at high temperatures occur with measurable velocities, and that velocities increase with increase in temperature following the laws of chemical kinetics, except that in these adsorption processes an activation energy is involved.

Taylor and Sickman,<sup>88</sup> studying the adsorption of hydrogen by zinc oxide at 184°C., found that 7.7 cc. of hydrogen were adsorbed on 20 grams of zinc oxide within one hour at N.T.P. and calculated the activation energy to be 13,500 calories per molecule, considering the temperature coefficient in the range 132° to 184°C.; this energy is equal to the energy with which a gas molecule strikes the surface when adsorption takes place. Taylor calculated from the kinetic theory using the formula:

$1/4(N/V)W_e^{E/RT}$ , where  $N/V$  denotes the number of molecules per cc., and  $W$  the velocity of the molecules, the number of molecules of hydrogen striking the zinc oxide surface/unit area/second, and found this to be about  $2 \times 10^{21}$  molecules/sq. cm./sec. This is about ten times the amount actually adsorbed by the total zinc oxide surface. Taylor concluded that molecules having the necessary activation energy are primarily adsorbed on the surface and that the surface contributes this energy.

The experiments of Taylor and Strother<sup>88a</sup> have shown that the velocity of hydrogen adsorption is a function of the surface and that activation energy is determined by the nature of the surface, the activation energy increasing with an increase in the surface covered.

Table 19.

Surface Covered Catalyst	Activation Energy (Kg. Cals.)	Activated Adsorption cc./100 g. of the Catalyst
ZnO	7-15	8.0- 24.0
ZnO—Cr <sub>2</sub> O <sub>3</sub>	1-12	40.0-120.0
ZnO—Mo <sub>2</sub> O <sub>3</sub>	17-33	0.4- 8.5

Burrage opposed Taylor's viewpoint regarding the possibility of measuring the energy of activation by rates of adsorption. He is of the opinion that activation energies may be derived from kinetics only for perfectly clean surfaces (not only must the surface be evacuated, but repeatedly flushed with the reaction gas at a high temperature). Kingman,<sup>40</sup> studying the heat of activation for adsorption catalysis of hydrogen on charcoal, recommends flushing charcoal with hydrogen at 400° to 500°. He found the activation heats practically constant over the entire range of adsorption, whereas Taylor found the heat of activation increased with increase in the volume adsorbed.

Garner<sup>25</sup> compared the heats of adsorption for hydrogen on various surfaces with their corresponding heats of activation as shown in Table 20 and found for all cases in which data are available that  $E < Q$ .

Table 20.

Gas	Surface	Heat of Adsorption (Q Calories)	Heat of Activation (E Calories)
Hydrogen.	Carbon	..	30
Hydrogen.	Al <sub>2</sub> O <sub>3</sub>	..	27.5
Hydrogen.	Cu	33	14.1
Hydrogen.	MnO	..	12.20
Hydrogen.	MnO·Cr <sub>2</sub> O <sub>3</sub>	20	6-10
Carbon monoxide.	Pd	15	7

The variation of activation energies for different surfaces was considered by Garner as indicating that it is not the electronic activation of adsorbed molecules which is involved, but the additional energy required for activation supplied either by the surface atoms or the surface atoms themselves are activated. The latter interpretation he considered the more plausible. Garner's viewpoint is in agreement with that of Taylor's, for it is known that the apparent activation energy of reactions proceeding in an adsorbed layer is in general different from the true activation energy.

Dohse and Kälberer,<sup>18</sup> investigating the decomposition of isopropyl

alcohol on bauxite inhibited by water proceeding as a unimolecular reaction expressed by the Polanyi-Hinshelwood equation:

$$E \text{ (observed)} = E \text{ (true)} + \lambda C_3H_7OH + \lambda H_2O$$

found the apparent activation energy to be 39,000 calories, while the true activation energy of the non-inhibited process (obtained either from a study of a zero order reaction by constant removal of the water vapor or by investigating at low surface concentration) gave a value of 26,000 calories. Further,  $\lambda C_3H_7OH$ , the heat of adsorption for low surface concentration, was found to be 21,000 calories;  $\lambda H_2O$ , 13,000 calories, and  $E \text{ (true)}$ ,  $39,000 + 21,000 - 13,000 = 47,000$  calories. Thus  $E \text{ (true)}$ , or 47,000 calories, is not in agreement with the 26,000 calories found for the non-inhibited zero order reaction. The discrepancy is even greater when it is considered that water vapor with a measured heat of adsorption of 13,000 calories inhibits the decomposition of isopropyl alcohol with a measured heat of adsorption or 21,000 calories. This has been considered proof that heat of adsorption is not a simple measure of the rate of evaporation. Dohse and Kälberer, therefore, concluded that to account for the inhibition by water in the present case an activation energy exceeding at least by 22,000 calories that of isopropyl alcohol must be assumed.

Temkin,<sup>89</sup> assuming that adsorption equilibrium is readily established in comparison with the velocity of the surface reaction, formulated a general equation relating the apparent activation energy to true activation energy in heterogeneous reactions.

Dew and Taylor<sup>11</sup> attempted to correlate the interrelationship between heat of activation, heat of adsorption, and catalytic activity by studying the adsorption of ammonia gas on copper, nickel, and iron catalysts. The relationship between heat of activation and heat of adsorption Hinshelwood<sup>34</sup> expressed by the equation:  $E_0 = E_t + \lambda' - \lambda$ , where  $E_0$  is the observed heat of activation;  $E_t$ , the true heat of activation;  $\lambda'$ , the heat of desorption, and  $\lambda$ , the heat of adsorption. Dew and Taylor obtained the heats of adsorption  $\lambda$  at very low partial pressures and found them to be as follows: (a) iron, 16,000 calories; (b) nickel, 11,300 calories, and (c) copper, 8,700 calories. These results have been considered indicative of the fact that the apparent heat of activation,  $E_0$ , would be most affected by the heat of adsorption in the case of iron and least affected in the case of copper. These investigators assume that the whole surface is not uniformly active and that it is the fraction of the surface which has the strongest adsorptive capacity that is the most active catalytically; the higher heat of adsorption of ammonia on iron is proof for the fact that for the corresponding catalytic reaction it is possible to raise an adsorbed molecule to a much higher temperature on an active iron spot than on an active copper spot. Therefore, there is greater possibility for interaction between the metal atom and the ammonia molecule for iron than for copper. Iron has a higher activity as a catalyst than copper for the decomposition of ammonia.

Dixon,<sup>18</sup> discussing the probability of using heats of adsorption and

heats of activation for predicting catalytic activity, is of the opinion that there are rather serious objections with respect to the assumption that true heat of activation is equal to the observed heat of activation minus heats of adsorption of the reactants.

Polanyi<sup>71</sup> postulated that heat of activation of a reaction can never be less than the heat of adsorption, while the heat of reaction can not be much higher than the heat of activation. In case the upper limits for the heat of reaction are not much higher than the lower limits given by the heat of activation, the heat of activation may even be equal to the heat of reaction.

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## Chapter 3

# Heterogeneous and Homogeneous Catalysis

### INTRODUCTION

Catalytic reactions may take place in heterogeneous or homogeneous systems. The conditions in the two cases are so different that they may well be used as a basis for classification.

In heterogeneous systems, the catalyst and the substance to be catalyzed are not in the same physical state; the catalyst may, for example, be a solid, while the reacting substances are gases or liquids. For a true homogeneous mixture, on the contrary, the catalyst and the reacting substances are not separated from each other by a phase boundary at which the catalytic reaction has its seat, both being uniformly distributed in the system.

In homogeneous systems, the catalyst functions in the form of single molecules, which are distributed among the molecules of the reactants, both being either a gas or a liquid, and having a mobility of the same order. The laws of thermodynamics and kinetics have been applied quite successfully to homogeneous systems, but in cases where several states of aggregation are involved the resulting complexities have prevented an equally complete solution. The state of substances at the boundary and within the phases is different with respect to concentration and mobility, as well as to the reactivity of the molecules. For the catalyzed reaction to take place, a molecular exchange between the phase boundary layer and the internal phase is required. To the chemical process of conversion of molecules in the boundary layer is added the physical process of diffusion. The conversion of the components in a system in the thin boundary cannot be measured directly; therefore, changes in amount in the internal phase are measured in time. In homogeneous catalysis the catalyst is maintained in an intimate mixture with the reacting components and is acting by its mass, so that in many instances, the velocity coefficient varies in direct proportion to the concentration of the catalyst. In such systems the efficiency of different catalysts may be compared by values for velocity coefficients, as these provide an accurate basis for estimating the relative activity.

In heterogeneous catalysis, where the catalyst is a solid and not in a true admixture with the reactants, the reaction velocity equation cannot be applied with sufficient accuracy because other factors, in addition to the mass action, are in control. The rate of action in heterogeneous reactions depends also on the rate at which the reacting components diffuse to the surface of the catalyst, are activated, and react, and the rate at which the product diffuses from the surface of the catalyst. Thus the

rate of heterogeneous reactions is directly proportional to the area of the exposed catalyst surface, while in the case of homogeneous reactions the concentration of the catalyst is the corresponding factor. In general, the velocity constants of heterogeneous reactions are characterized by smaller temperature coefficients than those for reactions in homogeneous systems. It is the critical increment,  $E$ , per gram molecule which is taken account of by the exponential term in the velocity expression  $e^{-E/RT}$  which governs the magnitude of the temperature coefficient of a reaction. The greater the value of  $E$ , the greater the temperature coefficient. On the other hand, the higher the critical increment the smaller the reactivity or the rate of the catalytic reaction.<sup>135, 136</sup>

A convenient classification of homogeneous catalysis appears to be first differentiating between gaseous and liquid systems and, secondly, subdividing the latter into (a) acid-, (b) base- and (c) salt-catalysis. Heterogeneous catalysis may be studied in conjunction with types of reactions such as oxidation, hydrogenation, polymerization, and others, which are influenced by contact substances of definite characteristics.

#### HETEROGENEOUS CATALYSIS

The types of catalytic reaction which have been applied commercially on a large scale as industrial processes correspond, in a great majority of cases, to heterogeneous systems. Although catalytic reactions of this type have already been discussed in previous chapters, nevertheless a few specific cases of heterogeneous catalytic reactions will be developed here in order to show the marked contrast between heterogeneous and homogeneous systems. To interpret the accelerating action of catalysts in heterogeneous systems, various mechanisms have been proposed, namely, (1) the catalyst is intermittently oxidized and reduced,<sup>22</sup> (2) the electrons emitted from the catalyst ionize the gases (reacting components), enabling them to react;<sup>130</sup> (3) the reaction components are adsorbed on the catalyst, whereby the faster conversion is achieved either as a result of an increase in their concentration,<sup>84, 94, 95, 203</sup> or of transmission in a medium of higher reaction velocity; and (4) a change takes place in the molecular state of the reacting components (formation of atoms).<sup>24, 222</sup> A most probable cause of the acceleration of the reaction was attributed by investigators to the adsorption of gases on the catalyst. In heterogeneous gas catalysis, for example, in the oxidation of sulfur dioxide to sulfuric acid, using different catalysts, such as platinum or the acids of vanadium and arsenic, the measured velocity is that velocity with which sulfuric acid diffuses through the layer of adsorbed sulfur trioxide, while the gases reaching the surface of the catalyst react almost instantaneously. In contrast to this group of heterogeneous catalyses, there is another group in which the reacting substance forms with an immeasurably high velocity an adsorption layer on the catalyst in which a chemical reaction takes place with a measurable velocity. The catalysis of detonating gas mixture on glazed porcelain is such an example (Bodenstein).

Hamburger<sup>107</sup> believed that heterogeneous catalytic behavior of metals is based on the action of surface electrons of the active metals and is



therefore related to their atomic structure. On the other hand, the tendency to form adsorption layers has also been considered, and the change in the activity of the catalyst assumed to be a function of the thickness of the adsorption layer.

Rideal,<sup>182</sup> discussing adsorption and the reaction ability in the case of heterogeneous catalysis, attributes the contact action to the formation of molecular surface layers on the catalyst as a result of adsorption. If substances participating in a reaction are concentrated through adsorption on an adsorbent, then the possibility of the reaction being accelerated may be anticipated. When such an acceleration is actually produced, the adsorbent may be considered a heterogeneous catalyst. Likewise, heterogeneous catalysis may be deduced from the adsorption phenomena. Therefore, the specific character of heterogeneous catalysts is related to their selective adsorption ability. Although in heterogeneous catalysis adsorption of one or more of the reacting components is the primary step, the accelerating effect cannot be explained solely by the increase in the active mass of the reacting components in the boundary, but is determined adequately by the orientation of the reacting elements in the boundary. Kruyt and van Duin<sup>135, 136</sup> are convinced that the orientation of molecules in the contact layer proposed by Langmuir<sup>141</sup> and Harkins,<sup>109</sup> is fundamental for all specific actions in the interface related to heterogeneous catalysis.

Kruyt opposed Bayliss' assertion<sup>17</sup> regarding heterogeneous catalysis and particularly with reference to the action of enzymes brought about by the surface condensation of the reacting constituents, due to intimate contact with and acceleration by mass action, by assuming that the influence exercised by an enzyme or a catalyst is based on an action which brings the reacting substances into a position advantageous for their interaction. Kruyt sought confirmation for his point of view in the reaction of  $\alpha$ ,  $\beta$ -dibromopropionic acid and potassium iodide resulting in the formation of acrylic acid, potassium bromide and iodine, charcoal being used as an adsorbent-catalyst and water as a medium. That an accelerating effect may be expected from a suitable aliphatic substance, such as  $\alpha$ ,  $\beta$ -dibromopropionic acid, in the case of charcoal rather than for sulfonated aromatic compounds, has been proved experimentally by Kruyt and van Duin<sup>5, 137</sup> on the basis of Harkins' theory.

$$K_1 = 0.000123, \text{ without charcoal}$$

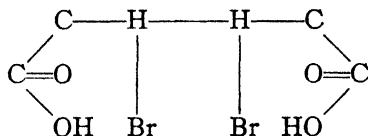
$$K_2 = 0.000149, \text{ with charcoal}$$

According to the latter, the chain of carbon atoms lies parallel to the contact surface, while the polar groupings are directed toward water. A positive contact catalysis can be expected only in case the reacting group is turned away from the adsorbent toward the surrounding liquid. In the present case, all electrically polar groups are turned toward water. The position of the polar groups in  $\alpha$ ,  $\beta$ -dibromopropionic acid is, however, not symmetrical, but it may be possible that the carboxyl group exerts a greater influence on orientation than the bromine atoms and, consequently, the latter are not in a favorable position to act. Kruyt

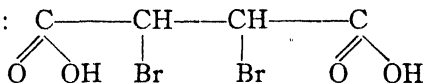
is of the opinion that better results can be expected with dibromosuccinic acid and potassium iodide, and that a comparison between this acid in solution and when adsorbed shows this clearly:

Dibromosuccinic acid:

(a) in solution:

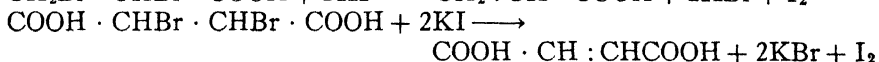
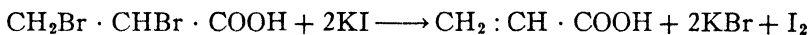


(b) when adsorbed:



In the first case, the molecule is to be considered as almost closed, while in the second case, the bromine atoms are more readily available for a reaction. Favorable orientation relationships obviously lie in the inversion of cane sugar by hydrochloric acid and in the saponification of esters when catalyzed by charcoal.<sup>134</sup>

According to Kruyt and van Duin, the stereochemical configuration suggests a still better arrangement in the case of the *meso*-form than in the case of the racemic.



Experimental evidence indicates a great catalytic acceleration of the reactions, fully supporting the theory.

It has been the belief of Garner<sup>96</sup> and Garner and Blench<sup>97</sup> that in heterogeneous catalysis not only the position and mode of orientation in the boundary, but also the energy content of the atoms forming the surface of a catalyst very largely determine the role they play as individuals in the catalytic process. Contrary to the simple reactions between oxygen and charcoal in the case of suitable heterogeneous catalysis are the labile fixed atoms of the catalyst surface whose relative positions, with respect to one another, may change during the reaction and which do not leave the surface and form possible acceleration centers by virtue of their high energy content. Garner states that if a part of the heat liberated during the heterogeneous reaction is adsorbed by the surface, not only an increase in the total surface, but also an increase in the number of active atoms exposed on the surface may result, and this indicates an increase in free surface energy per square centimeter.

A study of the mechanism of heterogeneous catalysis may be undertaken either by investigating the kinetics of the reaction or attempting to resolve the course of the reaction into well-defined, single chemical processes. While the first method credits the experimentally observed velocity values to the co-action of single molecular phenomena, such as collision, adsorption, desorption, rearrangement accounting for their frequency of occurrence, and balance of energy, the second method gives no

clue regarding the origin of velocities, but does explain the physico-chemical nature of these single phenomena.<sup>91, 92, 93</sup> Sauter,<sup>204</sup> reviewing the literature on heterogeneous catalysis, considered as significant for catalytic activity chemisorption and places of high energy content on the adsorbent. Sauter<sup>185</sup> considered heterogeneous catalysis as relating to chemical sorption. Haber<sup>106</sup> emphasized as significant in heterogeneous catalysis the position of the molecules in the catalytically active layers, relating it to conceptions in quantum mechanics. The proximity of the molecules in the adsorption layer is especially important in quantum mechanics because at shorter distances the resonance relations between the molecules may become more intimate.

Dohse and Kälberer<sup>69</sup> interpreted the heterogeneous decomposition of isopropyl alcohol on bauxite, according to the equation  $\text{C}_3\text{H}_7\text{OH} \longrightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O}$ , as a continuous adsorption reaction of the surface layer, whereby the catalyst surface is decreased by the adsorption of the water formed. The activation heat is equal to 39,000 calories. In the removal of the water and the slowing down of the reaction by barium oxide, the reaction becomes of a zero order, and the activation energy drops to 26,000 calories. The difference of 13,000 calories corresponds to the desorption heat of water. In studying the catalytic decomposition of hydrogen iodide at a gold surface heated between 500° and 800°, Hinshelwood and Prichard<sup>120</sup> ascertained that it is not influenced by the presence of hydrogen and is almost independent of the hydrogen iodide pressure, the reaction therefore being of the zero order. The rate of adsorption does not change with the temperature of the catalyst surface, and the activation heat is calculated from the temperature coefficient to be 25,000 calories per mol. On the other hand, the homogeneous decomposition of hydrogen iodide had an activation heat equal to 44,000 calories. This result led the investigators to the conclusion that activation heats of corresponding heterogeneous and homogeneous reactions are approximately in the ratio 1 : 2 and that while the homogeneous reaction is bi-molecular, the heterogeneous reaction proceeds monomolecularly.

Spitalsky and Kagan<sup>196</sup> applied the concepts of electronic polarization to the interpretation of the mechanism of heterogeneous catalysis. Pisarsjewsky<sup>166</sup> construed the mechanism of heterogeneous catalysis, referring to the surface layers of metal catalysts, as those with not fully constructed electronic groups so that a durable transition of electronic isomers (passive and active) into one another takes place. Balandin,<sup>13, 14</sup> in his model of dehydrogenation catalysis, illustrated heterogeneous catalytic reactions by applying his multiplet hypothesis, stating that the binding between atoms is broken if they are attracted by two different catalyst atoms. According to Balandin's hypothesis, catalysis arises through geometrically determined action of various catalyst centers. Furthermore, Balandin,<sup>15</sup> studying dehydrogenation of cyclohexane and alcohol in the presence of palladium with and without exposure to the ultraviolet radiation from a mercury lamp, stated that by illuminating the catalytic surface with ultraviolet radiation, which quanta are larger than those corresponding to the activation heat of the catalytic reaction, no acceleration of the

reaction follows. Also an inactive catalyst does not become active under the action of the radiation. The properties of the exposed surface and the velocity of energy transition in the respective heterogeneous catalysis account for the effect obtained. Franck's<sup>89</sup> quantum mechanical interpretation of heterogeneous catalysis implies that the latter follows through a transition in which the potential threshold is not exceeded by the activation heat, but whereby the potential barrier is penetrated. The probability of the transition in this process Franck considers as being favored by the proximity of molecules in the adsorbed state and by flattening of the potential walls.

According to wave mechanics, a wave assigned to an approaching atom does not need to pass over the energy barrier or wall; it may pass through the potential wall rather than over it, especially when the wall is thin and when beyond it is a state with similar energy to the one in front of it. According to Franck, the wave may prefer to go through a "tunnel" in the mountain rather than over it. That is why this theory of penetration of a potential barrier is called the "tunnel" theory.

Cremer and Polanyi<sup>55</sup> tested the "tunnel" theory of heterogeneous catalysis of styrene. It has been postulated that if hydrogenation occurs through the "tunnel effect," the velocity should be much smaller for the heavier than for the lighter hydrogen isotope, and when almost all the hydrogen has reacted the heavier isotope should be concentrated in the residue. Experiments failed to reveal this. Measurements of the displacement of the isotopic ratio actually should make it possible to decide whether the motion of atoms in chemical reactions can be represented by the equations of motion of classical mechanics or whether there are appreciable quantum mechanical deviations. Remesow,<sup>178</sup> discussing the possibility of applying the "tunnel effect" to catalytic hydrogenation, came to the conclusion that a considerable difference in reaction velocity should be found for the hydrogen isotopes. The experimental evidence for the catalytic hydrogenation of cholesterol on palladium gave, however, no proof of a tunnel effect. Remesow believes that, for proof of the latter, a refined method with accurate determination of isotopes is required.

Volmer<sup>213</sup> looks upon a chemical reaction as one in which velocity is defined as the number of germs formed in seconds per volume unit. This number of germs might be calculated relatively accurately at various degrees of supersaturation. Indicative of the velocity of germ formation is the expression: *e*-Potenz, which serves for its calculation. All factors which decrease the value of *e*-Potenz act catalytically upon the chemical reaction. It was from this point of view that Volmer attempted to differentiate homogeneous catalysis from heterogeneous catalysis. According to this viewpoint ions decrease the surface tension of the vapor phase and this effects the germ formation; in heterogeneous catalysis the germ formation is influenced by the walls of the container, this influence being greater for small angles between the droplets and the wall.

The germ formation is accompanied by a further precipitation of a new phase. In cases in which the molecules which are to form in the new phase must originate first by a reaction, two possibilities are assumed

by Volmer, namely, either the molecule formation occurs first and the origin of the new phase is determinative for the reaction velocity (homogeneous catalysis), or the molecule formation proceeds slowly, but is specifically catalyzed on the surface of the new phase (heterogeneous catalysis). For the energy transfer to single molecules in a reaction mixture reacting exothermally, it is known that the transference, as well as the giving off of excess energies, may follow through straight-line or branched propagation by reaction chains. Thus the products of an elementary process, charged with the liberated reaction energy, are capable of converting into a reactive state not only a single but two or more molecules. Chain reactions are known for ordinary chemical reactions, as well as catalytic reactions. In the first case the reaction-accelerating substances are formed from the initial substances of conversion, while in case of ordinary catalysis, there is no genetic relationship between the reaction-forwarding and the reacting substances; thus the accelerating agent remains materially unchanged in the course of the conversion. Christiansen and Kramers,<sup>51</sup> Christiansen,<sup>48, 49</sup> Christiansen and Huffman<sup>50</sup> and Ssemenoff<sup>200, 201, 202</sup> developed the theory of chain reactions estimating their kinetic character and providing a number of examples in heterogeneous catalysis confirming the existence of chains in them.

Christiansen<sup>48</sup> applied the theory of chain reactions for the interpretation of hydrogen action upon the decomposition of oxalic acid by sulfuric acid; likewise in the autoxidation of organic aldehydes by oxidizable substances or in the slowing down action of chlorine in the detonating gas reaction. Christiansen and Huffman<sup>50</sup> studied the reaction between methanol and water vapor as an example of heterogeneous catalysis. The kinetic investigation of the reaction:  $\text{CH}_3\text{OH} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + 3\text{H}_2$  was carried out at 190–250° with reduced copper as catalyst to which changing amounts of magnesium hydroxide were added. It has been found that methyl alcohol and hydrogen influence chiefly the velocity; methyl alcohol increases the latter, while hydrogen retards it. Christiansen,<sup>49</sup> interpreting the mechanism of this reaction, stated that the hindering action observed in this heterogeneous catalysis as a function of the adsorption displacement is not the only possible reason for it, and that a possibility may exist also that in the adsorbed layer, as well as in the gas phase, a reaction sequence may originate which is completed there, and is analogous to the one known in the kinetics of homogeneous systems.

Williams<sup>221</sup> studied the kinetics of thermal uniting of ethylene and bromine on glass surfaces at 0–25° under pressures of a few mm. to 100 mm. The reaction is heterogeneous and consists essentially in bromine addition. In certain cases, especially when an excess of bromine is present, an additional reaction, probably polymerization of intermediate products of bromination, takes place. Certain experimental results, such as strong dependence of the reaction velocity upon the bromine pressure, slowing down of the reaction by poisoned glass splinters and inert gases seemed to indicate a chain reaction in the gas space. The order of the reaction depends upon the reaction vessel and is 1 or 2, seldom 0. It has been found that by a given surface of the vessel the reaction order diminishes by in-

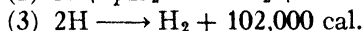
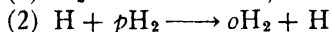
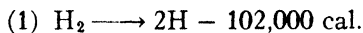
creasing pressure and dropping temperature. The reaction velocity constant is independent of ethylene pressure, but grows with the bromine pressure; an increase in the container's surface favors the reaction.

The velocity of ethylene bromide synthesis decreases with increasing temperature, which fact cannot be explained by the decrease in the concentration of the reaction partner in the adsorption layer. It is stated that the ethylene bromide reaction is accelerated by the addition of water, the effect becoming more pronounced as the quantity of water is increased. The transition of the reaction order from 2 to 1 is favored by a moistened vessel wall, high bromine pressure, and low temperature. It is believed that the function of water in this reaction consists in the formation of a bromine hydrate on the wall with which ethylene reacts further. Finally, addition of ethylene bromide acted in the sense of raising the velocity.

Bennewitz and Neumann<sup>21</sup> postulated a chain reaction mechanism for the catalytic hydrogenation of ethylene over platinum catalyst in spite of its endothermic character.

Foresti<sup>87</sup> constructed a special differential micro-calorimeter which permitted a direct measurement of the heat of reaction on a platinum catalyst. They found that in Bennewitz and Neumann's hydrogenation process of ethylene actually an exothermic reaction takes place upon the catalyst and that the heat developed (molecular heat of reaction about 30 K cal.) corresponds to about the one calculated for ethylene hydrogenation. Thus, according to Foresti, this heterogeneous catalysis occurs completely at the surface of the catalyst and the chain reaction mechanism proposed by Bennewitz and Neumann is thereby disproved.

It is to be remarked that although chain reactions are rather characteristic of the kinetics of exothermic reactions, chlordonating gas chains, chains of combustion processes, etc., reaction chains are fundamentally possible, as is also true in the case of endothermic processes insofar as the heat supply is steady and continuous. But the reaction chains in the case of endothermic reactions are never very long; they are limited and stationary, as the energy required for propagation of the chain is not produced out of itself, but requires a supply from the outside. A transition from endothermic to exothermic reaction chains represents the thermo-neutral chain of *para-ortho*-hydrogen conversion through hydrogen atoms:



The chain starts with a strongly endothermic initiating reaction (1) of hydrogen atoms. This partial process seldom continues because of the high activation energy required for it. Reaction (2) is thermo-neutral, and in reaction (3) the energy used up in (1) is regained. As a result of process (3), as well as the recombination at the wall, each hydrogen atom has a limited life span and converts therefore only a limited number of *para*-hydrogen molecules. The process as a whole is determined by the partial process (2) and therefore depends greatly on the concentration of hydrogen atoms in the stationary equilibrium. The *para*-hydrogen

conversion has been found to be better catalyzed by certain substances at high temperatures, while other substances exhibit a different behavior. Thus, for example, charcoal catalyzes well at the temperature of liquid air, while at lower temperatures it is inactive. On the contrary, platinum black catalyzes instantaneously at ordinary temperatures, but is inactive at the temperature of liquid air. At low temperatures, molecular oxygen adsorbed on charcoal accelerates catalysis.

Bonhoeffer, Farkas and Rummel,<sup>26</sup> who observed these effects, assumed that the difference in the temperature coefficient of catalysis was not responsible for this behavior of catalysts. Positive, as well as negative, temperature coefficients may be observed in the case of both catalyst groups, depending upon the temperature and the properties of the surface. In general, positive, as well as negative, temperature coefficients may be found for the same material. A positive temperature coefficient is found always above room temperature and a negative one only at low temperatures. These results have been interpreted by assuming that two different reaction mechanisms are in existence, namely, (1) at low temperature, in the field of monomolecular transformations of isolated hydrogen molecules, conversion occurs in the adsorption layer with a negative temperature coefficient of the catalytic process; and (2) at high temperature, in the field of activated adsorption, conversion results from desorption of the adsorbed atoms and their recombination to form new molecules.

The chain mechanism assumed by Kobosew and Anochin<sup>132</sup> for the catalytic oxidation of hydrogen at temperatures below 200° and, likewise, by Bennewitz and Neumann<sup>21</sup> for the hydrogenation of ethylene at ordinary temperature, has been criticized by Zeldowitsch and Roginsky,<sup>24</sup> who entertain the belief that there is no reason for assuming volume chains in the case of heterogeneous gas reactions in the low-temperature range, although the abnormally high velocities of such reactions appear to be reasonable according to molecular kinetic conceptions, taking into consideration the activation and adsorption heats, as well as isotherms, of the reacting compounds.

In studying the heterogeneous-homogeneous hydrogen-oxygen catalysis in the presence of platinum in a round vessel at 80 mm. mercury pressure and volume ratio of  $H_2 : O_2 = 1.5 : 4.1$ , Poljakow, Stadnik and Elkenbard<sup>172</sup> and Poljakow and Stadnik<sup>171</sup> obtained a maximum in the formation of a detonating gas mixture ( $H_2 : O_2 = 2 : 1$ ) and the evidence of a space reaction with indications that its mechanism is independent whether it has an explosive or a heterogeneous-homogeneous character. The dependence of hydrogen peroxide formation on the temperature of platinum catalyst (350–400°) was related to differences in the number of initial centers, which determine the stationary or explosive character of the process. The dependence of the detonating gas mixture catalysis on the total and partial pressure, as well as on the form and size of the container used for the reaction, indicates the fact that the space reaction represents a chain process. In further investigations<sup>167, 168, 169, 170</sup> it has been found that by increasing the diameter of the container the formation of a detonating gas mixture decreases, which was interpreted by assuming

that the reaction took place at the wall of the container ( $M$ ) according to the equation:  $2OH + M \longrightarrow H_2O_2 + M$ , the space reaction forming hydroxyl molecules which represent the most important members of the chain mechanism—as in the explosion, so in the corresponding space catalysis.

A similar mechanism was proposed for ozone formation according to the equation:  $O + O_2 + M \longrightarrow O_3 + M$ , the oxygen atoms in space being members of the chain mechanism. Thus the formation of a detonating gas mixture follows obviously by the splitting up of the chain at the cold walls of the reaction container. It has been shown also that the formation of a detonating gas mixture on the platinum surface, being a volume process and having a chain character, may be confirmed by actually showing that the chains are broken off. Experiments were carried out by surrounding the platinum wire catalyst with a platinum net, with the result that while in the ordinary reaction the yield of the detonating gas mixture increased with increase in temperature and either the breaking off of a member of the chain or a discontinuing of the volume process, in the present case no detonating gas mixture was obtained.

Prettre's<sup>174, 175, 176</sup> kinetic investigation of a thermal chain reaction in the case of a hydrogen-oxygen mixture showed the influence of pressure, temperature, concentration and inert gases upon the velocity of the homogeneous reaction between hydrogen and oxygen in the temperature interval 540–580° in a "Pyrex" vessel, with and without its walls covered with potassium chloride, and obtained results indicating a chain mecha-

Table 1. Heterogeneous Catalysis in Gas Reactions.

Reaction	Catalyst	Observer
Decomposition of nitrogen oxydul * ( $N_2O$ ); temperature 1000–1800°.	Glowing Pt.	Cassel and Gluckauf: <i>Z. physik. Chem. (B)</i> , <b>9</b> , 427–36 (1930).
Heterogeneous gas reactions.		Topley: <i>Nature</i> , <b>128</b> , 115–16 (1931).
Heterogeneous catalysis of binary gas reactions.		Kröger: <i>Z. anorg. allgem. Chem.</i> , <b>205</b> , 369–97 (1932); refer also to Constable: <i>Proc. Cambridge Phil. Soc.</i> , <b>29</b> , 291–306 (1932). Mitchell: <i>J. Chem. Ed.</i> , <b>9</b> , 261–71 (1932).
Heterogeneous conversion of CO into $CO_2$ ; reaction believed to proceed in three steps (side reactions play a small part). (1) $O_3 \rightarrow O_2$ , adsorbed. (2) $O_2$ adsorbed accumulates. (3) $O_2$ adsorbed + $2CO \rightarrow 2CO_2$ . On the active catalysts the activation of oxygen is assumed to occur through an intermittent reduction and oxidation of the catalyst.	$Cr_2O_3$ , $ZnO$ , $Al_2O_3$ , $Fe_2O_3$ (activation heat between 25 and 26 K cal./mol). $CuO$ , $MnO_2$ (activation heat 8–10 K cal./mol).	Finkelstein, Rubanik and Chrisman: <i>Zhur. Fiz. Khim.</i> , <b>3</b> , 425–38 (1933).
Heterogeneous catalysis of gas reactions.	Metal oxides.	Pourbaix: <i>Bull. soc. belge ing. ind.</i> , Nr. 7/8, p. 67 (1934).
Heterogeneous catalysis of gas reactions; for a definite reaction an oxide pair serves as catalyst, which $O_2$ equilibrium pressure is equal at the corresponding temperature to the $O_2$ pressure of the gas mixture to be catalyzed.	Two various oxidation stages of a metal or the metal and its oxide; both are present in an oxidation-reduction equilibrium with $O_2$ .	Pourbaix: <i>Rev. universelle mines (8)</i> , <b>11</b> (78), 367–70 (1935).



nism. The velocity of this reaction has been expressed by the following equation:

$$W = K[H_2]^2[O_2] \cdot pe^{-95,000/RT}$$

where  $p$  is the pressure of the gas mixture. The application of Bursian and Sorokin's<sup>44</sup> formula to the velocity of a chain reaction in the scheme proposed by Bonhoeffer and Haber<sup>26</sup> led to a similar expression:

$$W = K'[H_2]^2[O_2]pe^{(E_1+E_2)/RT}$$

where  $E_1$  is the activation energy of the reaction:  $H_2 + O_2 \longrightarrow 2(OH)$  and  $E_2$  the activation energy of the reaction:  $OH + H_2 \longrightarrow H_2O + H$ . If the experimentally measured velocity is introduced into this formula, then for  $E_1 + E_2$  a value of 86,500 cal. instead of 95,000 cal. is obtained, assuming that the difference between these two values lies within experimental error and confirms Haber's scheme for the chain reaction. Prettre, in discussing the results which he obtained by comparing glass covered and not covered with potassium chloride, found that the clean glass walls

Table 2. Heterogeneous Catalysis in Various Reactions.

Reaction	Catalyst	Observer
Micro-heterogeneous decomposition of $H_2O_2$ ; ultra-filtrated iodine sols much more active in comparison with the initial sol; catalytic action of iodine sols based on rapid adsorption of $H_2O_2$ on colloidal particles of iodine.	Iodine sol (cholesterin); cholesterol ester and lecithin in colloidal state, not active.	Remesow: <i>Ber.</i> , <b>67</b> , 134-40 (1934).
Heterogeneous catalysis of cyclohexane on charcoal covered with Ni containing adsorbed $H_2$ ; a weaker adsorption of cyclohexane takes place on charcoal alone whereby cyclohexane decomposes, and the adsorption of $H_2$ apparently does not influence the decomposition.	Charcoal covered with Ni (1.01%) (24 hrs. shaking of coal with a solution of 0.2% $Ni(NO_3)_2$ , drying and reduction in $H_2$ stream); activated with $H_3PO_4$ .	Storfer: <i>Z. Elektr.</i> , <b>41</b> , 198-204 (1935).
Heterogeneous reaction between benzyl chloride and solid $AgNO_3$ at about 35°; reaction velocity dependent only on the surface of used $AgNO_3$ but independent on the amount of benzyl chloride.	$AgNO_3$ ( $H_2O$ acts preventive upon the reaction already in amount 0.18% related to the weight of benzyl chloride).	Nabar and Wheeler: <i>Proc. Indian Acad. Sci. (A)</i> , <b>2</b> , 265-78 (1935).
Heterogeneous catalytic decomposition of ethyl alcohol.		Balandin: <i>Zhur. Fiz. Khim.</i> , <b>7</b> , 655-58 (1936).
Heterogeneous catalysis (course, increase of direct current resistance of metal powders).		Reichardt: <i>Z. Elektr.</i> , <b>39</b> , 289-306 (1931).
Heterogeneous catalysis in copper-copper oxydul systems (rectifying action).		Ostwald and Erbring: <i>Kolloid Z.</i> , <b>57</b> , 7-14 (1931).
Heterogeneous formate formation.		Birstein and Lobanow: <i>Z. anorg. allgem. Chem.</i> , <b>195</b> , 173-194 (1931).
Heterogeneous catalysis.		Roginsky: <i>Zhur. Fiz. Khim.</i> , <b>6</b> , 249-54 (1933); refer also to Ljubarski: "Heterogeneous Catalysis," Goschimtechisdat, Moscow-Leningrad, 1933.
Heterogeneous catalytic hydrogenation.		Schmidt: <i>Chem. Rev.</i> , <b>12</b> , 363-417 (1933).
Stereo-isomeric conversion of oximes as an example of heterogeneous catalysis.		Taylor and Lavington: <i>J. Chem. Soc. (London)</i> , <b>1934</b> , 980-987.

adsorb considerable amounts of hydrogen as well as water vapor between 500–600°. The velocity of adsorption is rather small, but increases with rise in temperature. In investigating the influence of these active adsorptions upon the velocity of the detonating gas mixture reaction, it has been ascertained that water vapor adsorption strongly accelerates the reaction and contributes to it an autocatalytic character, while hydrogen adsorption on the contrary slows down the conversion without influencing the character of the chain, leading to the disappearance of the induction period and showing a strong increase in the velocity during the first few minutes. The potassium chloride-covered glass walls adsorb both hydrogen and water vapor, but less intensively than glass not so covered. Prettre states that under a pressure of 400–700 mm. and in the vicinity of the ignition point, the reaction velocity does not conform to Arrhenius' law, but increases rapidly with increasing temperature. It is said that under these conditions a homogeneous, many-branched chain process takes place, causing an explosion.

### HOMOGENEOUS CATALYSIS

When all the participants of a reaction, including the catalyzing agent, are in one and the same state of aggregation and in the same phase, the system is homogeneous. There are two types of homogeneous systems, namely, homogeneous gas catalysis which is accelerated through gaseous catalysts, and homogeneous liquid catalysis in which a solute is used as a catalyst. Many systems appear to be of a pseudo-homogeneous character or actually heterogeneous, because of the possibility of partial processes at the walls of the container, on liquid drops, or on dust particles.

### Homogeneous Gas Reactions

For simple gas reactions, it is postulated that two gas particles  $A$  and  $B$ , mixed together in concentrations  $C_A$  and  $C_B \left( \frac{\text{Mol}}{\text{cm}^3} \right)$  at a temperature  $T$  may react only when they collide. The number of these collisions is  $NZC_AC_B$  per volume unit in a second:

$$Z = 2\sigma^2 N \sqrt{2\pi RT \frac{M_A + M_B}{M_A M_B}}$$

where  $N$  is the number of molecules per mol;  $R$ , the gas constant;  $M$ , the molecular weight, and  $\sigma$  equals  $\sigma'10^{-8}$  cm.—the sum of radii of  $A$  and  $B$ .

Thus  $Z \sim 3.10^{12} \sqrt{\frac{M_A + M_B}{M_A M_B}} T \sigma'^2$ .

Only a fraction of the total number of collisions results in a reaction, and this fraction is determined by three factors:

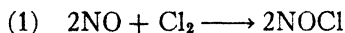
(1) The steric factor reflecting the geometric configurations and relationships between particles.

(2) The factor which expresses the influence of specific heats (rotation and vibration).

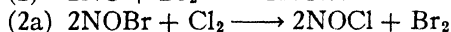
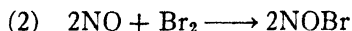
(3) The factor expressed in the form  $e^{-Q/RT}$  originated because a collision, in order to be effective, requires a minimum energy, designated

by  $Q$  and called the heat of activation. Only a few molecules possess a sufficient energy at low temperatures to react, but with increasing temperature the number of active molecules increases greatly. The first two factors are smaller than one, but they change the order of magnitude by two tenths. The third factor is the essential one. On the other hand, it must be considered that each reaction has its own activation heat and its own counter reaction, which in the equilibrium state has equal velocity. If the conversion  $A + BC \longrightarrow AB + C$  has the heat evolved in the reaction  $Q$ , and the activation heat of the reaction  $q_1 = A + BC$  and that of the counter reaction  $AB + C \longrightarrow A + BC$  is  $q_2$ , then  $-Q = q_1 - q_2$ . The difference in activation heats of the reaction and counter reaction is equal to the heat evolved in the conversion (Trautz's rule).<sup>209, 210</sup>

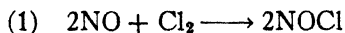
Herzfeld,<sup>113, 114</sup> discussing the decomposition of chlorine into atoms and the chlorination through atoms, assumes that the substance that is chlorinated takes up all free chlorine atoms or serves as an acceptor for them, whereby the catalyzing of chlorine decomposition means catalyzing of the chlorination process. Instead of one direct step from the initial to the final substance, there are two steps, the first from the starting substance to the intermediate product, the second from the intermediate to the end product. In this sequence the velocity of the slower stage is the rate determining factor for the entire process. Thus for catalysis to occur it is necessary that the slower of the two partial reactions proceeds faster than the initial reaction. The favorable condition is about equal velocity of both partial reactions. On the other hand, the slower partial reaction is that with the higher activation heat and for catalysis to occur, it is necessary that for a not too small concentration of the catalyst the activation heat of the intermediate product should be considerably smaller than that of the initial substance. In a favorable case the heat of activation of the former is about half that of the latter. Thus Herzfeld attempted to formulate quantitatively the conditions for substances which may be used as intermediate reaction catalysts. An example of intermediate product catalysis in homogeneous gas reactions is the NOCl formation through  $\text{Br}_2$  and  $\text{NO}_2$ . It seems to occur in a direct way:



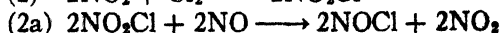
over NOBr as a catalyst



Reactions (1) and (2a) determine the velocity of NOCl formation, and reaction (2) regulates the catalyst concentration. The same is ascertained in catalysis of NOCl formation in the presence of  $\text{NO}_2$  as catalyst. The direct reaction is



while with  $\text{NO}_2\text{Cl}$  as a catalyst



Reactions (1) and (2a) again indicate the velocity of NOCl formation and (2) regulates the catalyst concentration.

Opposite to the chemical conception with respect to homogeneous gas reactions was the physical conception advocated by Tramm,<sup>208</sup> who believed that the manner of action of a catalyst consists not in initiating a new reaction course, namely, that of reaction components entering into intermediate combinations with the catalyst, but that the catalyst action is rather expressed in a change of the tracks of valence electrons thereby facilitating the chemical transformations. The sources of the activation energy are: the kinetic energy of colliding molecules, the dark radiation of the reaction space, and the heat evolved in the process. By producing spectral lines through collisions with rapidly moving atoms and molecules, it was found that only the non-elastic collisions are essential in activation.<sup>90</sup> It is assumed that in case of non-elastic collisions the electron orbits of colliding molecules undergo changes due to which energy may be given off. In order that a chemical reaction may take place, the atoms within the molecules have to undergo certain rearrangements during their collisions. These rearrangements are actually the changes in the state of atoms and molecules, which energy changes are between quantized values. From the point of view of some investigators the elementary changes in the state of atoms and molecules during processes of activation and inactivation, as well as during the elementary chemical reactions are those of greatest importance in homogeneous systems.<sup>3, 131</sup>

Molecules built up of a great number of atoms or atomic groups may be considered to be capable of carrying out a whole series of intermolecular vibrations corresponding to the number of their degrees of freedom,  $n$ , and thus have the ability to store activation energy. According to Lindemann,<sup>148</sup> the fraction of active molecules with  $n$  degrees of freedom is:

$$\frac{e^{-A/RT} \cdot \left(\frac{A}{RT}\right)^{(1/2n-1)}}{(1/2n-1)}$$

and the equilibrium ratio for active molecules is considerably greater than for simply built molecules (with  $n = 2$ ). If, for example, the activation energy of a reaction is  $A = 20,000$  cal., then at  $500^\circ$  absolute the fraction of active molecules is for:

$n = 2$	$n = 4$	$n = 6$	$n = 8$	$n = 10$
$10^{-8.6}$	$20 \cdot 10^{-8.6}$	$200 \cdot 10^{-8.6}$	$1333 \cdot 10^{-8.6}$	$6660 \cdot 10^{-8.6}$

From the above relationship, one may obtain the expression involving the temperature coefficient of the reaction velocity:

$$A = RT^2 \frac{d \ln K}{dT} + (1/2n - 1) \cdot RT$$

Table 3 shows the activation expressed in freedom degrees for different examples.

In order to account for the rate of a reaction of complex molecules

Table 3.

Decomposition	Activation freedom degrees	Observer
$\text{CH}_3\text{—N=N—CH}_3$	25	Ramsperger: <i>J. Am. Chem. Soc.</i> , <b>49</b> , 912, 1495 (1927).
$\text{CH}_3\text{—N=N—C}_3\text{H}_7$	33	Ramsperger: <i>Ibid.</i> , <b>51</b> , 2134 (1929).
$\text{C}_3\text{H}_7\text{—N=N—C}_3\text{H}_7$	>40	Ramsperger: <i>Ibid.</i> , <b>50</b> , 714 (1928).
$\text{CH}_3\text{—N=N—NH—CH}_3$	>14	Ramsperger: <i>Ibid.</i> , <b>50</b> , 714 (1928).
$\text{N}_2\text{O}$	~30	Daniels and Johnston: <i>Ibid.</i> , <b>43</b> , 53 (1921). Ramsperger and Tolman: <i>Proc. Nat. Acad. Sci. U. S.</i> , <b>16</b> , 6 (1930). Schumacher and Sprenger: <i>J. Am. Chem. Soc.</i> , <b>16</b> , 129 (1930). Kassel: <i>Ibid.</i> , <b>52</b> , 3972 (1930).
$\text{C}_2\text{H}_5\text{—CHO}$	11	Hinshelwood and Thompson: <i>Proc. Roy. Soc. London (A)</i> , <b>113</b> , 221 (1926).
$\text{C}_2\text{H}_5\text{—O—C}_2\text{H}_5$	6–8	Hinshelwood and Thompson: <i>Ibid.</i> , <b>114</b> , 84 (1927).
$\text{CH}_3\text{—O—CH}_3$	11–12	Hinshelwood and Thompson: <i>Ibid.</i> , <b>115</b> , 215 (1927).
$\text{CH}_3\text{—O—C}_2\text{H}_5$	9	Glass and Hinshelwood: <i>J. Chem. Soc. (London)</i> , <b>1929</b> , 1805.
$\text{CH}_3\text{—O—C}_3\text{H}_7$	12	Glass and Hinshelwood: <i>Ibid.</i> , <b>1929</b> , 1809.
$\text{CH}_3 \cdot \text{COCH}_3$	—	Hinshelwood and Hutchinson: <i>Proc. Roy. Soc. London (A)</i> , <b>111</b> , 245 (1926).
$\text{N}_2\text{O}$	2	Volmer and Kumerow: <i>Z. physik. Chem. (B)</i> , <b>9</b> , 141 (1930). Nagasako and Volmer: <i>Ibid.</i> , <b>10</b> , 414 (1930). Nagasako and Volmer: <i>Ibid.</i> , <b>11</b> , 420 (1931). Volmer and Bogdan: <i>Ibid.</i> , <b>21</b> , 257 (1933). Volmer and Froehlich: <i>Ibid.</i> , <b>19</b> , 85 (1932). Volmer and Briske: <i>Ibid.</i> , <b>25</b> (1934).

in homogeneous gas systems, the Maxwell-Boltzmann law for the distribution of energy may be applied in the form appropriate to many degrees of freedom. In fact, in the decomposition of certain organic compounds many internal vibrations must be assumed to participate in the activation process. A more marked correlation between the structure of the molecule and the kinetic character of its reaction is in existence in the case of molecules of a complex structure than in the case of simple molecules. Lindemann postulated the existence of a time lag between activation and transformation, which can be considered as an essential condition for the reaction. The simplest kind of homogeneous reaction is probably the bimolecular reaction in a gas, where it may be that nothing more is required for a chemical change than an impact of sufficient violence between two molecules.<sup>116, 146</sup> The distinction between unimolecular and bimolecular reactions has been traced back to that of degrees of freedom only. For example, the decomposition of ozone shows many signs of being of an intermediate character. It is predominantly bimolecular,<sup>223</sup> but several degrees of freedom are involved.<sup>20</sup> In ordinary molecular

nitrogen both atoms are so tightly bound to each other that they show only little inclination to join other elements, while in the compounds of nitrogen with other elements the bond is less strong; therefore the nitrogen element has a greater freedom and possesses a reaction ability. The inactivity of nitrogen is thus of a completely different nature from that of noble gases. The inactivity of molecular nitrogen is not due to the lack of affinity of its atoms for those of other elements, but rather to their remarkable attraction for each other. The homogeneous gas reaction between nitrogen and hydrogen proceeds very slowly. Measurable reaction velocities are obtained only in a heterogeneous reaction by using suitable contact substances, such as metallic catalysts, which obviously activate the nitrogen and the hydrogen, either through the formation of intermediate products or through condensation of the mono-atomic active parts of both gases at their surface.

In specific molecular actions, a particularly marked influence of identical molecules upon one another is often observed. As an example of this may be quoted the decomposition of acetaldehyde in the gaseous state.<sup>119</sup> This is a bimolecular reaction and the decomposition depends upon a collision between two aldehyde molecules. Collisions with hydrogen or with nitrogen molecules also provoke decomposition, but are much less effective than the collisions between the like molecules. The quantum mechanical interpretation of this fact assumes a kind of resonance phenomenon in which there is a marked coupling of two atoms at distances considerably greater than the ordinary molecular diameter.<sup>117</sup>

The kinetics of gaseous reactions in homogeneous systems has been an object of extensive investigation. Lindemann's theory<sup>148</sup> postulated that the molecules of a gas reacting at a rate proportional to the first power of its concentration are so constituted that after receiving a critical increment of energy through an unusually violent collision they must pass through some internal phase before the reaction occurs. Except at very low pressures the majority of activated molecules lose their extra energy by a second collision before the phase is complete. Therefore, although activated molecules are produced at a rate proportional to the square of the concentration, the number surviving to complete the internal phase and then to react is directly proportional to the concentration, provided that the time elapsing between activation and deactivation is small compared to that intervening between activation and reaction. Furthermore, when the pressure is too low for this condition to be fulfilled, the reaction will no longer be unimolecular and the ratio of the reaction velocity to concentration should drop with decreasing pressure.

Hinshelwood and Thompson<sup>121</sup> proved Lindemann's point of view for decomposition of gaseous propaldehyde following the unimolecular law at high pressure, but with a ratio falling off rapidly when the pressure is reduced below 80 mm. In the case of decomposition of dimethyl ether, the ratio falls off below 300 mm. and for decomposition of diethyl ether, the ratio falls off below 150 mm.<sup>118</sup> With all three substances, when a sufficient amount of hydrogen is added, it has been found that the velocity coefficient does not fall off with decreasing partial pressure of the reactants.

At higher concentration, however, the absolute value of the coefficient is not affected by the presence of hydrogen and therefore, according to Hinshelwood, hydrogen does not act chemically but merely by maintaining the Maxwell distribution of energy among the molecules of the reacting gas when the supply of activated molecules would otherwise begin to fall short of that required to keep the coefficient constant. The action of hydrogen is specific, because neither helium nor nitrogen shows the same effect.

The velocity constant of unimolecular decomposition in gaseous systems has been found<sup>181</sup> to be unaffected by the presence or absence of water vapor, nitric acid, or dust particles, and to be independent of the mode of preparation of the catalyst. Although Hirst and Rideal have stated that the velocity constant increases at very low pressures, the observation by Hibben<sup>115</sup> failed to confirm it, as he found the constant's value, ranging from 0.002 mm. to 0.2 mm. pressure, was the same as that found for normal pressure. Hinshelwood and his co-workers ascertained that unimolecular decomposition was more characteristic for substances such as nitrogen pentoxide, acetone (dimethylketone), diethylketone, and ethyl aldehyde, which have large molecules. Bimolecular constants were obtained for substances like hydrogen iodide, chlorine monoxide, and nitrous oxide, which have simple molecules. Due to a more complex structure, the first group required a longer time to elapse between activation and reaction. It thus appeared to Hinshelwood that the absolute value of the reaction velocity confirms the fact that complexity of structure is an essential factor in bringing about a unimolecular decomposition.

It has been suggested that for certain types of reactions at either end of a continuous range, unimolecular and bimolecular rates of decomposition may be expected. The appearance of the unimolecular type is favored by complexity of molecular structure and high pressures, while simplicity of structure and low pressures tend toward bimolecular reactions.

Christiansen<sup>47, 116</sup> has shown that in five of the six known examples of bimolecular gas reactions the rate of the reaction is given by the expression: number of collisions  $\times e^{-E/RT}$ , where  $E$  is the energy of activation. In the case of unimolecular reactions the actual rate of the reaction is many times larger than that given by the above expression.

It has been calculated that four modes of internal vibration may be involved in the decomposition of ether and six in that of propaldehyde. To account for this effect it has been shown<sup>88, 147</sup> that the internal degrees of freedom of molecules also have to be considered as contributing essentially toward the energy of activation.

Clusius and Hinshelwood<sup>84</sup> attempted to compare the activation heats of non-catalyzed and catalyzed reactions and found that the former have higher values than the latter and that the activation heats increase with increasing complexity of the molecule for the non-catalyzed and decrease for the catalyzed reaction.

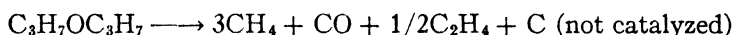
The decrease in the activation energy for the decomposition reactions as indicated in Table 4 in the presence of a catalyst has been interpreted in the sense that in the absence of a catalyst the ether molecules require

Table 4. Activation Heat in Kilogram Calories.

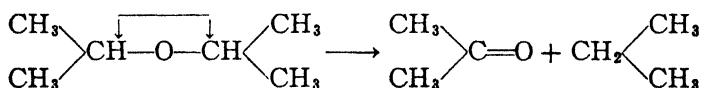
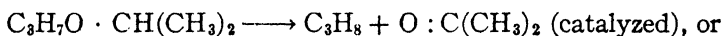
Substance Decomposed	Catalyzed	Non-Catalyzed
Dimethylether.	—	65
Methylethylether.	38	47
Diethylether.	34	53
Diisopropylether.	28.5	60.5
Acetaldehyde.	32.5	45.5
Nitrogen monoxide.	35.5	54

for their decomposition an agitation corresponding to at least 13 degrees of freedom. Likewise, the energy of transition lies upon numerous single bonds capable of vibrating, whereas under the action of the catalyst iodine an activation of only one single degree of freedom of the ether molecules is required.

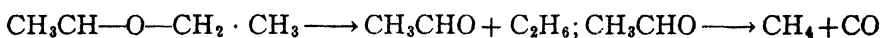
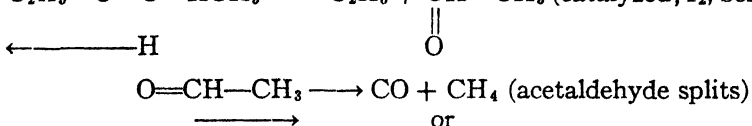
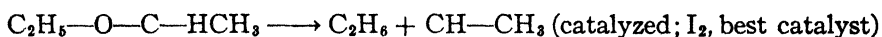
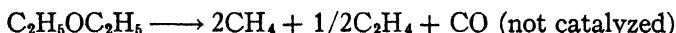
Hinshelwood and his co-workers studied catalyzed gas reactions of organic compounds as examples of pure homogeneous catalysis with regard to the possible mechanism by which the reaction proceeds and with special emphasis on the acceleration factor of the reaction velocity. It has been proved in certain homogeneous catalytic decompositions that the initial step in the reaction is the migration of a hydrogen atom from carbon to oxygen. Thus, for example, Glass and Hinshelwood<sup>99</sup> proved that diisopropylether is decomposed at 550° in a homogeneous reaction:



In the presence of iodine vapors, this ether is split catalytically at 400° in an easily measurable reaction of the first order. The homogeneous decomposition catalyzed by iodine proceeds in a completely different manner from the one catalyzed by iron and may be expressed as follows:



This reaction takes place also under the influence of alkali iodides and to a smaller extent with the alkyl bromides and hydrogen bromides; the chlorides act very little.<sup>52, 53</sup> Another example is the decomposition of diethylether. The catalyzed and non-catalyzed reactions give different products:



Iodine shows a strong catalytic influence on the homogeneous decom-





be in equilibrium with hydrogen molecules. Every type of these catalytic homogeneous gas reactions postulates definite requirements for their occurrence.

In some of the homogeneous catalyses of organic gas reactions the velocity is proportional to the catalyst concentration; in others, it reaches

Table 6. Homogeneous Catalysis in Gas Reactions.

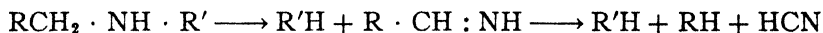
Reaction	Catalyst	Observer
<b>Catalysis of nitrosylchloride formation.</b>	Br <sub>2</sub> .	Kiss: <i>Rec. trav. chim.</i> , <b>43</b> , 68-70 (1923).
(1) $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$ (direct)	NOBr intermediate compound.	Kiss: <i>Chem. Weekblad.</i> , <b>24</b> , 466 (1927).
(2a) $2\text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$		
(over NOBr catalyst)		
(2b) $2\text{NOBr} + \text{Cl}_2 \rightarrow 2\text{NOCl} + \text{Br}_2$		
(3a) $\text{Cl}_2 + \text{Br}_2 \rightarrow 2\text{ClBr}$		
(3b) $2\text{ClBr} + 2\text{NO} \rightarrow 2\text{NOCl} + \text{Br}_2$		
<b>Homogeneous catalysis of the <i>para-ortho</i> hydrogen conversion:</b> $\text{pH}_2 + \text{X} \rightleftharpoons \text{oH}_2 + \text{X}$ (X = paramagnetic collision partner) temperature $\sim 600^\circ$ .	Paramagnetic gases: O <sub>2</sub> , NO, NO <sub>2</sub> .	Farkas and Sachse: <i>Z. physik. Chem. (B)</i> , <b>10</b> , 419 (1930); <b>23</b> , 1-18 (1933); <i>Preuss. Akad. Wiss.</i> , 268-79 (1933). Geib and Harteck: <i>Z. physik. Chem.</i> , (Bodenstein Festband), 849 (1931).
Conversion of <i>para</i> H <sub>2</sub> to <i>ortho</i> H <sub>2</sub> (the reaction passes through an intermediate stage in which the H—H bond is loosened and the molecule split); synthesis of water from H <sub>2</sub> and O <sub>2</sub> ; activation energy for water formation, 18 K. cal.; for the atomic exchange between H <sub>2</sub> and water vapor, the activation energy is small—6 K. cal.	Crystals of phthalocyanine or copper-phthalocyanine (a few mg.); activation energy for phthalocyanine = 5,700 and for copper phthalocyanine = 5,000 cal.; the same catalyst catalyzes other reactions.	Calvin, Eley and Polanyi: <i>Trans. Far. Soc.</i> , <b>32</b> , 1436-1443, 1443-1446 (1936).
<b>Decomposition of N<sub>2</sub>O into nitro- gen and oxygen.</b>	Halogen atoms, not mole- cules, act as catalysts.	Hinshelwood and Musgrave: <i>Proc. Roy. Soc. London (A)</i> , <b>135</b> , 23 (1932); <b>137</b> , 25 (1932).
<b>Catalysis of decomposition of N<sub>2</sub>O by mercury vapor.</b>	Mono-atomic gas.	Volmer and Bogdan: <i>Z. physik. Chem. (B)</i> , <b>21</b> , 257 (1933).
<b>Decomposition of di-isopropyl ether:</b>	Isopropyl iodide (small amounts), or iodine.	Glass and Hinshelwood: <i>J. Chem. Soc. (London)</i> , <b>1929</b> , 1815.
$  \begin{array}{c}  \text{CH}_3 \quad \quad \quad \text{CH}_3 \\  \diagdown \quad \quad \diagup \\  \text{CH} - \text{O} - \text{CH} \\  \diagup \quad \quad \diagdown \\  \text{CH}_3 \quad \quad \quad \text{CH}_3  \end{array}  \rightarrow  $ $  \begin{array}{c}  \text{CH}_3\text{CH}_2 - \text{CH}_3 + \text{CH}_3 - \text{CO} - \text{CH}_3 \\  \text{propane} \qquad \qquad \text{acetone}  \end{array}  $ <p>at 400°C.</p>		
<b>Decomposition of di-isopropyl ether:</b>	Alkali iodides, alkyl bromides and hydrogen bromide.	Clausius and Hinshelwood: <i>Z. Elektr.</i> , <b>36</b> , 743-49 (1930); <i>Nature</i> , <b>125</b> , 311 (1930); <i>Proc. Roy. Soc. London (A)</i> , <b>128</b> , 75 (1930); <b>128</b> , 82 (1930). Clausius: <i>J. Chem. Soc. (London)</i> , <b>1930</b> , 2607.
$  \begin{array}{c}  \text{CH}_3\text{CH} - \text{O} - \text{CH}_2\text{CH}_3 \rightarrow \\  \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{I} \\  \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}  \end{array}  $		
<b>Decomposition of ether</b> $(\text{C}_2\text{H}_5)_2\text{O} \rightarrow 2\text{CH}_4 + 1/2 \text{C}_2\text{H}_4 + \text{CO}$ T. 700-1000°; reaction, homoge- neous; consists in condensation of active molecules.	Pt or W.	Taylor: <i>J. Phys. Chem.</i> , <b>35</b> , 1044-53 (1931).
<b>Catalytic decomposition of diethyl ether at 498-607°.</b>	NO.	Staveley and Hinshelwood: <i>Proc. Roy. Soc. London (A)</i> , <b>154</b> , 335-48 (1936).

Table 6 (Continued).

Reaction	Catalyst	Observer
Catalytic decomposition of methyl-ethyl ether followed by a monomolecular decomposition of acetaldehyde; ethane is considered a further primary decomposition product.	Alkyl halide, $I_2$ .	Urea and Young: <i>J. Phys. Chem.</i> , <b>37</b> , 1183-90 (1933).
$C_2H_6 \rightleftharpoons C_2H_4 + H_2$ .		
Catalytic decomposition of acetaldehyde, propionaldehyde, $n$ - and isobutyraldehyde; catalytic decomposition of esters: methyl formate and methyl acetate.	$I_2$ .	Baird and Hinshelwood: <i>J. Chem. Soc. (London)</i> , <b>1933</b> , 1147-55, 1155-60. Baird: <i>Trans. Far. Soc.</i> , <b>29</b> , 1127 (1933).
Catalytic decomposition of simple aliphatic amines: diethylamine, triethylamine.	$I_2$ (molecules).	

an upper limit. In all reactions catalyzed by iodine, a hydrogen atom is displaced and a bond is broken. The activation energy of the catalyzed reaction is in general much smaller than that of non-catalyzed reactions and appears to be localized in the part of the molecule where it is most active with respect to the resolution of the binding. The selective energy displacement seems to be favored by the polarization and attraction of iodine molecules.<sup>11</sup> Hinshelwood especially emphasized a relationship between the properties of organic compounds catalytically split and those of the catalysts performing the acceleration in the gas reactions. In the case of ethers, esters, and amines, the dipole moment is localized in bonds split by the catalytic decomposition. The ease of polarization of the catalyst is considered to be essential. However, it has been found that in the decomposition of acetaldehydic substances pyridine and sulfur dioxide, which have a high polarization, do not act as catalysts. It was assumed that intermediate compounds formed between such a catalyst and acetaldehyde are too stable, preventing a rapid completion of the cycle. Hinshelwood supposed that by coming close to the dipole of the molecules of the reactant, as a result of polarizing ability of the halide molecules, an induced dipole moment is obtained and a short living dipole aggregate is formed with the colliding partner. In the collision complex a transition of vibration energy from the catalyst molecule to the double bond of the organic reacting molecules takes place readily and completely on account of a favorable mutual orientation.

The structural similarity between  $C-O-C$  and  $C-NH-C$  is expressed also in a certain analogy of the catalytic decomposition of amines and ethers because they both react according to scheme:

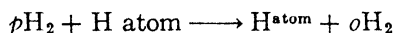


In the case of methyl compounds, hydrogen and therefore hydrogen iodide may originate, which reduces some of the amines. The hydrogen bound to nitrogen plays no essential part because it has been found that triethylamine and diethylamine both are catalyzed to a comparatively equal degree.<sup>12</sup>

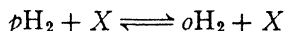
In the second type of homogeneous catalysis in the gaseous state the acceleration of the splitting process of  $N_2O$  into nitrogen and oxygen by means of halogen atoms is not proportional to the pressure of catalyzing

halide molecules, but increases proportionally to the square root of the pressure, thus following the same law as the amount of halide atoms which stand in a thermal equilibrium with halogen molecules present in the gaseous space. The decomposition of  $N_2O$  by mercury vapor is an example involving a monoatomic gas. Volmer and Bogdan<sup>214</sup> showed that the rate of the reaction is directly proportional to the concentration of the catalyst (pressure of mercury vapor).

The homogeneous catalysis of the *para-ortho*-hydrogen conversion by paramagnetic gas molecules, such as oxygen, nitric oxide and nitrogen peroxide, constitutes the third example of simple homogeneous gas catalysis. Without a catalyst this reaction proceeds in a gas space as follows:



Farkas and Sachse<sup>85, 86, 98</sup> studied catalysis of  $pH_2 \longrightarrow oH_2$  conversion in a gas space and showed that *para*-hydrogen converts into *ortho*-hydrogen without the presence of hydrogen atoms at very low temperatures in the presence of paramagnetic molecules (likewise paramagnetic ions in solution). Even at room temperature an essential fraction of collisions leads to the molecule conversion according to the scheme:



where  $X$  equals the collisions of the paramagnetic molecule. The mechanism of action consists in cancelling of the normally inhibited *para*  $\rightleftharpoons$  *ortho* transition through a specific magnetic field originating by collision with the paramagnetic partner. The reaction with oxygen or nitric oxide, is homogeneous, proceeds bimolecularly and according to the first order. It is temperature-dependable with collision yields of about  $10^{-12}$  on the average. The experimentally determined velocity may be calculated from properties of reacting and catalyzed molecule types. The two kinds of hydrogen molecules differ only in regard to nuclear spin; the nuclei of *ortho*-hydrogen spin in an anti-parallel manner, while *para*-hydrogen spins with parallel motion. The reaction velocity is measured in broad intervals. The small temperature dependence of the collision yield and the absolute velocity of the reaction agree well with the theoretical conceptions developed by Wigner. The *para-ortho* conversion occurs also in solvents, such as water, aniline, benzene, methyl alcohol and cyclohexanol, but the constant of the reaction velocity is only  $5 \times 10^{-6}$  times that for the gas reactions. The conversion in these cases is ascribed to the action of the hydrogen atoms in the solvent molecules upon the *para*-hydrogen molecules. In the aqueous half-molar solutions of the bivalent sulfates of zinc, copper, nickel, cobalt, iron and manganese, with magnetone number varying from 0 to 5 in the series, the conversion velocity of the *para*-hydrogen  $\rightarrow$  *ortho*-hydrogen progresses in the same sequence ( $Zn = O$ ,  $Mn$  is about 5 times that for  $Cu$ , etc.). The collision yield is about 10 times higher than in the reactions in the gas space and becomes greater with decrease in the concentration of the salt solution. In connection with this, Wigner calculated the probability of *para-ortho*-hydrogen conversion as the result of an exchange action of the nuclear spin with the inhomogeneous

magnetic field of the collision partner and found that it equals  $2\mu s 5\mu p^2 I / -9h^2 A_s^2 RT$ , where  $\mu s$  and  $\mu p$  denote the magnetic moments of the collision partner and the proton moment respectively;  $I$ , the inertia moment of hydrogen, and  $A_s$ , the distance in the case of collision. Experiments with ions of the iron group and with ions of rare earths showed that through them the conversion of  $pH_2 \rightarrow oH_2$  is caused in the same manner as with paramagnetic gases. In the iron group the reaction velocity increased with increasing magnetic moment and increasing dilution of the ion, while in the case of the rare-earth ions, it is independent of the dilution. The magnetic collision distances decrease here with the increasing order number. In water saturated with  $pH_2$  and  $O_2$ , the constant of the reaction velocity at  $20^\circ$  is  $10.5 \text{ Mol Min}^{-1}$ , which is in good agreement with the constant for gas reaction found to be  $9.16 \text{ Mol Min}^{-1}$ .

### Homogeneous Liquid Reactions

Homogeneous reactions in solids are rarely known; chemical changes involving solids usually occur at their surface, as well as from nuclei of a newly formed phase where a combination of a chemical change and a crystal growth phenomenon takes place,<sup>128</sup> the only remaining variety of homogeneous systems in catalysis is that in which all the components are in a liquid state or in solution (refer to Tables 7-13).

It has been proposed<sup>184</sup> to classify homogeneous catalysis into direct or chemical and indirect or medium catalysis. According to this conception a direct catalyzer does not appear in the stoichiometric equation and its influences depend on the formation of intermediate molecular complexes, while the indirect catalyzer influences the velocity of the reaction by affecting the particular conditions upon which the given reaction depends, such as formation of complexes or their dissociation. The nature of the medium, *i.e.*, the solvent, is the factor that is considered to influence the conditions of the catalytic reaction. While a direct catalyzer is assumed to obey the law of chemical mass action because it reacts chemically, the indirect catalyzers, which may be practically all the participants, are subject to a different interpretation. According to Rosanoff's assumption, the relative change of the velocity coefficient of a reaction is proportional to the change in the concentration of the indirect catalyzer. Rosanoff, generalizing the conception of solvent influence, expressed it mathematically by the equation:  $d\ln K/dC = K$  (constant). If  $K = K_0$  when  $C = 0$ , then on integration  $K = K_0 e^C$ . If different concentrations for all substances present are considered, then the expression changes to:

$$K = K_0 e^{K_1 C_1 + K_2 C_2 + K_3 C_3}$$

in which case  $K_0$  is the reaction velocity freed from the influence of the medium. The equilibrium constants of a particular reaction will not be the same in various solvents. While the number of indirect catalyzers is large for any given reaction and may act positively or negatively, the direct catalyzers are confined only to positive action (because governed by the law of mass action).

In the kinetics of homogeneous catalytic reactions Hinshelwood<sup>116</sup> considers various solvents from the general point of view as homogeneous catalysts. In connection with the quantitative kinetics, the knowledge of the number of collisions between solute and solvent molecules has been considered of importance, and Moelwyn-Hughes<sup>156a</sup> developed a formula for the calculation of this number, which gives a reciprocal relation between viscosity (the collision number is assumed proportional to viscosity) and the diffusion coefficient:

$$D = RT/6\pi\eta rN$$

Table 7. Homogeneous Catalysis in Liquid Reactions (Oxidized by Air).

Reaction	Catalyst	Observer
Oxidation of aqueous ammonia by air.	Small amounts of a Cu salt.	Loew: <i>J. prakt. Chem.</i> (2), <b>18</b> , 298 (1878).
Oxidation of sodium sulfite, urea, creatin, asparagine, glyccoll.	Cu salts.	
Oxidation of tartaric acid and carbohydrates.	Cu in Fehling's solution (rather an induced reaction).	
Oxidation of acetaldehyde to acetic acid.	Silicic acid or blood coal containing Fe; acetates of Fe, Mn, U, Ni, Cr and V <sub>2</sub> O <sub>5</sub> , CeO, Fe <sub>2</sub> O <sub>3</sub> .	G.P. 261,589. G.P. 286,400.
Oxidation of high molecular weight liquid paraffinic hydrocarbons, e.g., pentane and hexane, also mixtures such as benzine, petroleum and paraffin by air or oxygen to form fatty acids and other oxidation products (in addition to CO and CO <sub>2</sub> , a mixture of aldehydes, ketones and fatty acids is obtained).	Stearates, palmitates, resinates of Fe, Co, Mn, Ce, Pb and V.	Franck: <i>Chem. Ztg.</i> , <b>44</b> , 309, 742 (1920). Grun: <i>Ber.</i> , <b>53</b> , 987 (1920).
Oxidation of glucose in alkaline solution by air.	Ce(OH) <sub>2</sub> .	Engler and Weisberg: "Kritische Studien der Autoxidation," 1904. Job: <i>Compt. rend.</i> , <b>134</b> , 1052 (1902); <b>136</b> , 45 (1903); <i>Ann. chim.</i> (7), <b>20</b> , 207 (1900). Goard and Rideal: <i>Compt. rend.</i> , <b>1</b> , 1560 (1924). Spoehr: <i>Compt. rend.</i> , <b>2</b> , 937 (1924).
Oxidation of amino compounds, likewise ethyl and methyl amines.	Cu compounds.	Traub: <i>Ber.</i> , <b>37</b> , 3130 (1904); <b>39</b> , 166, 178 (1906). Wieland and Beyel: <i>Ann.</i> , <b>439</b> , 196 (1924).
Drying or solidification of oils, especially linseed oil, by air.	Oleates, linoleate, resin-ate of Mn, Pb; more seldom that of Co, V, U.	Kissling: <i>Z. angew. Chem.</i> , <b>4</b> , 395 (1891). Lippert: <i>Z. angew. Chem.</i> , <b>11</b> , 412 (1898). Weger: <i>Chem. Rev. Fell-Harz-Ind.</i> , <b>4</b> , 301 (1899). Geuthe: <i>Z. angew. Chem.</i> , <b>19</b> , 2087 (1906).
Oxidation of benzaldehyde to benzoic acid.	Fe compounds.	Baeyer and Villiger: <i>Ber.</i> , <b>33</b> , 1569 (1900). Kuhn and Meyer: <i>Naturwiss.</i> , <b>16</b> , 1028 (1928).
Homogeneous catalytic oxidation of benzene (conc. of benzene-620 mm. Hg); T = 433°.	Ethyl nitrate, 0.1% conc.	Griffith and Hill: <i>Trans. Far. Soc.</i> , <b>32</b> , 829-36 (1936).
Oxidation of anthracene in aqueous alkali suspension or in pyridine solution under pressure at 170° by air to anthraquinone.	CuO.	G.P. 292,681.
Oxidation of aqueous solutions of leucine, glyccoll, alanine and other albumins by air.	H <sub>2</sub> containing Fe.	Handovsky: <i>Z. physiol. Chem.</i> , <b>176</b> , 79 (1928).

Table 8. Homogeneous Catalysis in Liquid Reactions (Oxidized by Chemically-bound Oxygen).

Reaction	Catalyst	Observer
Oxidation of certain ketones.	HNO <sub>2</sub> .	Behrend and Schmitz: <i>Ann.</i> , <b>277</b> , 313 (1893). Behrend and Tryllar: <i>Ann.</i> , <b>283</b> , 210 (1894). Kiliani: <i>Ber.</i> , <b>54</b> , 456 (1921).
Oxidation of polyvalent alcohols to oxaldehydes and oxyketones by H <sub>2</sub> O <sub>2</sub> .	Metal salts.	Fenton and Jackson: <i>J. Chem. Soc.</i> , <b>65</b> , 899 (1897); <b>75</b> , 1575 (1899). <i>Chem. News</i> , <b>78</b> , 78 (1898). Neuberg: <i>Ber.</i> , <b>35</b> , 962 (1902).
Oxidation of glycol and glycerol (5 and 6 valent alcohols) to the corresponding sugars by H <sub>2</sub> O <sub>2</sub> .	Metal salts.	Morell and Crafts: <i>J. Chem. Soc.</i> , <b>77</b> 1219 (1900).
Oxidation of wood to oxalic acid; 60-70% HNO <sub>2</sub> .	Nitrates of Fe, as well as rare earths.	Frankenburger: "Katalytische Umsetzungen," Leipzig Akademische Verlags Gesellschaft, m.b.H., 1937.
Oxidation of cane sugar to oxalic acid by HNO <sub>2</sub> .	V and Mo compounds.	Neumann, Moeser and Lindenbaum: <i>J. prakt. Chem.</i> (2), <b>75</b> , 148 (1907). G.P. 228,664. G.P. 329,591.
Titration of oxalic acid by KMnO <sub>4</sub> .	Mn <sup>+</sup> salts.	Frankenburger: "Katalytische Umsetzungen," Leipzig Akademische Verlags Gesellschaft, m.b.H., 1937.
Kjeldahl nitrogen determination by oxidation of organic compounds by conc. H <sub>2</sub> SO <sub>4</sub> .	Hg, Cu, Pt, Mo compounds.	Bredig and Brown: <i>Z. physik. Chem.</i> , <b>46</b> , 502 (1903). Rosenthal: G.P. 127,179. G.P. 127,180.
Oxidation of H <sub>2</sub> by conc. KMnO <sub>4</sub> solution (quantitative oxidation).	Small amounts AgNO <sub>3</sub> .	Hein and Daniel: <i>Z. anorg. allgem. Chem.</i> , <b>181</b> , 78 (1929).
Oxidation of aromatic hydrocarbons by HNO <sub>3</sub> ; benzene to picric acid and o-nitrophenol.	Hg salts.	Frankenburger: "Katalytische Umsetzungen," Leipzig Akademische Verlags Gesellschaft, m.b.H., 1937.
Oxidation of benzene homologs, e.g., toluene to aldehydes and acids by hypochlorites.	Ni, Mn compounds.	G.P. 127,388. G.P. 377,110.
Oxidation of benzene to pyrocatechin by H <sub>2</sub> O <sub>2</sub> (OH groups introduced into the benzene nucleus).	Metal salts.	Cross, Bevan and Heiberg: <i>Ber.</i> , <b>33</b> , 2015 (1900).
Oxidation of benzene to benzoquinone and maleic acid by H <sub>2</sub> O <sub>2</sub> .	Cu, Ag oxides and Ce compounds.	Kempf: <i>Ber.</i> , <b>38</b> , 3963 (1905); <b>39</b> , 3715 (1906).
Oxidation of naphthalene by H <sub>2</sub> SO <sub>4</sub> to phthalic acid.	Hg salts.	Sapper and Brunck: "Entwicklung der Indigo-fabrikation," <i>Ber.</i> , <b>33</b> , (1900). G.P. 91,202.
Oxidation of naphthalene by H <sub>2</sub> SO <sub>4</sub> to phthalic acid.	Ce, La and other rare earths, as well as a mixture of Cu and Hg salts.	Ditz: <i>Chem. Ztg.</i> , <b>29</b> , 581 (1905). Bredig and Brown: <i>Z. physik. Chem.</i> , <b>46</b> , 502 (1903).
Oxidation of anthracene in suitable solvents (acetic acid, nitrobenzene, chlorobenzene) by HNO <sub>3</sub> or HNO <sub>2</sub> to anthraquinone, or in H <sub>2</sub> SO <sub>4</sub> solution to oxyanthraquinone.	Hg salts.	G.P. 284,083. G.P. 284,179. G.P. 153,129 (1903). G.P. 161,954 (1904).
Oxidation of anthraquinone by H <sub>2</sub> SO <sub>4</sub> to hydroxylated derivatives.	Hg salts or selenic acid.	Schmidt: G.P. 162,035.
Oxidation of o- and p-toluidine by nitrobenzene (Couper's method) to form fuchsine.	FeCl <sub>3</sub> , V compounds.	Häussermann: "Industrie der Teerfarbstoffe," Stuttgart, 1881. Schmidt and Bahlsperger: <i>Ann.</i> , <b>233</b> , 339 (1899).
Oxidation of acridine to acridone by chloride of lime.	Salts of hypochloric acid.	Pictet and Patry: <i>Ber.</i> , <b>26</b> , 1962 (1893).

Table 8 (Continued).

Reaction	Catalyst	Observer
70,000 parts aniline oxidized to aniline black by sodium chlorate or $K_2Cr_2O_7$ .	One part V salt. Addition of a promoter aromatic amine, such as <i>p</i> -diaminobenzene or <i>p</i> -amidophenol activate the V compounds so that oxidation proceeds satisfactorily in air.	Sabatier and Witz: Green: E.P. 16,189 (1907).
Oxidation of aniline by $H_2SO_4$ .	Selenic acid.	Mohrmann: <i>Ann.</i> , <b>410</b> , 377 (1915). Holdermann: <i>Ber.</i> , <b>39</b> , 1253 (1906).
Oxidation of <i>o</i> - and <i>p</i> -nitraniline to <i>o</i> - and <i>p</i> -dinitrobenzene by $H_2O_2$ .	Cu, Ag oxides and Ce compounds.	Witt and Kopetschini: <i>Ber.</i> , <b>45</b> , 1134 (1912).
Oxidation of dimethyl aniline by chromates or chlorates to methyl violet.	Cu salts.	Frankenburger: "Katalytische Umsetzungen," Leipzig Akademische Verlags Gesellschaft, m.b.H., 1937.

Table 9. Homogeneous Catalysis in Liquid Reactions (Chlorination).

Reaction	Catalyst	Observer
Synthesis of higher hydrocarbons from halogen alkyl and aromatic hydrocarbons.	$AlCl_3$ .	Friedel and Craft: <i>Compt. rend.</i> , <b>84</b> , 1392, 1459 (1877); E.P. 4769 (1877). ( <i>Nouv. Ser.</i> ), <b>27</b> , 482 (1877); <i>J. prakt. Chem.</i> , <i>N(F)</i> , <b>16</b> , 233 (1877); <i>Rev. Ser.</i> , <b>820</b> (1878). Gustavson: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>9</b> , 287 (1877) <i>Ber.</i> , <b>10</b> , 1180 (1877); <b>11</b> , 2151 (1878); <i>J. prakt. Chem.</i> , <b>34</b> , 161 (1886). Friedel and Bahlsohn: <i>Bull. soc. chim.</i> , <b>35</b> , 52 (1881). Ulich and Heyne: <i>Z. Elektr.</i> , <b>41</b> , 509 (1935).
$C_6H_6 + RX \rightarrow C_6H_5R + HX$ .		
Preparation of acid chlorides (phosgene) and aromatic hydrocarbons.	$AlCl_3$ .	Gatterman: <i>Ber.</i> , <b>28</b> , 2869 (1895). Kränzlein: Berlin, 1930.
$R \cdot CO \cdot X + C_6H_6 \rightarrow RCO_2C_6H_5 + HX$ .		Jacobsen: <i>Compt. rend.</i> , <b>84</b> , 1392 (1877).
Preparation of benzene from toluene.	$AlCl_3$ .	Anschütz: <i>Ber.</i> , <b>18</b> , 339 (1885).
$C_6H_5CH_3 + HCl \rightarrow C_6H_6 + CH_3Cl$ .		
Synthesis of imido ketones by condensation of nitriles and phenols.	$ZnCl_2$ .	Hoesch: <i>Ber.</i> , <b>48</b> , 1122 (1915). Slater and Stephen: <i>J. Chem. Soc.</i> , <b>117</b> , 309 (1920).
Catalytic condensation of benzyl chloride with toluene.	$AlCl_3$ .	Steele: <i>J. Chem. Soc.</i> , <b>83</b> , 1470 (1903).
Friedel-Craft synthesis (traces of metal halides are probably formed).	$FeCl_3$ , $ZnCl_2$ , $SbCl_5$ , $P_2O_5$ .	Friedel: <i>Ann.</i> , <b>159</b> , 367 (1871). Elbs: "Syntetische Darstellungsmethode der Kohlenwasserstoffe," Band II, Leipzig, 1891. Comstock: <i>J. Am. Chem. Soc.</i> , <b>18</b> , 547 (1896). Lecher: <i>Ber.</i> , <b>46</b> , 2664 (1913).

Table 10. Homogeneous Catalysis in Liquid Reactions (Sulfurization).

Reaction	Catalyst	Observer
Sulfurization of aromatic hydrocarbons.	Hg salts, V salts.	Fischer, E.: "Einleitung zur Darstellung org. Präparate," 8te Auflage. Dimroth: <i>Ber.</i> , <b>31</b> , 2154 (1898); <b>32</b> , 758 (1899); <b>35</b> , 2032, 2853 (1902); <b>40</b> , 2411 (1907). Iljinsky: <i>Ber.</i> , <b>36</b> , 4194 (1903). Schmidt: <i>Ber.</i> , <b>37</b> , 66 (1904). G.P. 149,801. G.P. 157,123.

Homogeneous liquid reactions have been studied in aqueous alcoholic and etheric media which, on account of high dielectric constants have strong dissociating and solvating effects. Indifferent solvents, such as aliphatic and aromatic hydrocarbons, carbon tetrachloride, etc., offer less



Table 11. Homogeneous Catalysis in Liquid Reactions (Diazotation).

Reaction	Catalyst	Observer
Diazotation of amino naphthol.	Cupric salts.	G.P. 171,024. G.P. 172,446. G.P. 175,593. G.P. 178,621. G.P. 178,936.

Table 12. Homogeneous Catalysis in Liquid Reactions.

Reaction	Catalyst	Observer
Complex homogeneous catalysis of $\text{H}_2\text{O}_2$ .	Na molybdate.	Spitalsky and Funk: <i>Z. physik. Chem.</i> , <b>126</b> , 1-23 (1926); <i>J. Russ. Phys.-Chem. Soc.</i> , <b>60</b> , 47-74 (1928).
Stereoisomeric conversions of oximes.	$\text{LiCl}$ , $\text{KCl}$ , tetramethyl ammonium chloride in alcohol (K acetate, K ethyl sulfate have no influence).	Taylor and Roberts: <i>J. Chem. Soc.</i> , <b>1933</b> , 1439-44.
Catalytic decomposition of acrolein at 358-418° and 40-553 mm. initial pressure, in the catalytic reaction the temperature required is more than 100° lower.	$\text{I}_2$ .	Thompson and Frewing: <i>Trans. Far. Soc.</i> , <b>31</b> , 1660-68 (1935).
Homogeneous reactions; reduction ability of $\text{H}_2$ for $\text{H}_2\text{SO}_4$ greatest with 800 mg. $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ in 100 cc. $\text{H}_2\text{SO}_4$ (smallest amount of the catalyst that gives highest effect in conc. $\text{H}_2\text{SO}_4$ ).	$\text{HgSO}_4$ , $\text{CuSO}_4$ , $\text{AgSO}_4$ , $\text{TeO}_2$ , $\text{SeO}_2$ .	Milbauer: <i>Coll., trav. chim. Tcheco-slovaque</i> , <b>8</b> , 543-54 (1936).
Kjeldalization of saccharose (50 mg.) through 100 cc. conc $\text{H}_2\text{SO}_4$ at 302° gave a velocity limit in the presence of: 0.640 g. $\text{TeO}_2$ } 0.1929 g. $\text{V}_2\text{O}_5$ } 0.960 g. $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ } 1.8 g. $\text{HgSO}_4$ }	V and Mo oxides in $\text{H}_2\text{SO}_4$ were reduced and acted catalytically in the manner of Pt metals.	

complex conditions. There is a very intimate association between the solvent and the reacting components of a system. Sometimes the solvent molecules exert an activating, sometimes a deactivating influence. The solvent may have an enormous influence causing the velocity of the reaction to vary over a range of a thousandfold.<sup>146</sup> It has been proved<sup>152</sup> that the decomposition of nitrogen pentoxide takes place at the same rate in carbon tetrachloride solution as in the gaseous state. Likewise, the racemization of pinene proceeds with the same velocity in solution and as a pure liquid as it does in a gaseous state.<sup>153</sup> On the other hand, the bimolecular reactions studied by Christiansen<sup>46</sup> and Norrish and Smith<sup>158</sup> proceeded much slower in solutions than in the gaseous state. The deactivating effect has been interpreted in the sense that the effectiveness of bimolecular collisions between molecules appeared to be ten to several times smaller in the presence of a solvent.

In considering the total effect of a reaction acceleration in homogeneous catalysis in solution, recognition must be given to inorganic electrolytes, such as acids, bases and salts, as well as undissociated organic molecules and organic dissociation products. In solving the problem concerning the mechanism of the accelerating influence exercised by inorganic and organic ingredients upon conversions carried out in solutions in case of homogeneous systems, it is important to know whether the specific effect is due to their ionic or molecular state and the manner in which the accelerating effect is brought about with respect to different catalytic

reactions. Therefore, homogeneous catalysis in solution may be subdivided into: (1) specific inorganic and organic acid and specific inorganic and organic base catalysis; (2) catalysis in which both acid and base catalysts are at the same time suitable for one and the same reaction; (3) anion and cation catalysis, and (4) co-action of ions and undissociated molecules—catalysis in which the "salt effect" is well expressed.

Ostwald<sup>161</sup> found that the affinity constants of a series of 34 acids as deduced from experiments on the homogeneous catalysis of hydrolysis of methyl acetate and of the inversion of cane sugar corresponded to the electrical conductivities of the acids. Similarly, the velocities of saponification of ethyl acetate by 4 alkalies and 13 nitrogenous bases were related to the conductivities of these bases. Arrhenius' investigations<sup>7, 9, 10</sup> indicated likewise that the catalytic effect of acids and bases upon certain reactions in aqueous solutions is independent of individual chemical characteristics of these catalysts but is proportional to their degree of dissociation. The theory of electrolytic dissociation, finally developed in 1887, attributed the catalytic activity of acids and bases to the free  $H^+$  and free  $OH^-$  ions in solutions. Ostwald in his book<sup>162</sup> stated that the possibility of taking part in chemical reactions lies only in free ions and that the capacity of a reaction in a given solution is proportional to the number of free ions it contains. Van't Hoff<sup>211</sup> considered ions resulting from the electrolytic dissociation of an acid or base as active factors in catalysis. On the basis of Marcelin's explanation of the effect of temperature on the reaction velocity, Lambie and Lewis<sup>140</sup> suggested a radiation theory for the phenomena of catalysis in solutions. According to the latter, radiation is adsorbed and emitted only by charged vibrating particles. It is believed that the catalyzing ion is vibrating between neighboring molecules, mainly those of the solvent, and that the radiation emission is due to such vibrations, being similar to that obtained by vibrations of charged atoms in a solid such as a metal. On emitting radiation the ion loses energy, which it then regains from the surroundings; at any particular interval of time all the ions do not possess the same energy. Some have more, some less energy than the mean value. According to Marcelin, the catalytic effect is due to a localized increase in radiation density. In the case of hydrolysis of methyl acetate, the energy emitted by the vibration of a hydrogen ion is sufficient to supply the "critical increment" to the methyl acetate molecule in the amount of energy it needs to become active. The energy needed to decompose one molecule of methyl acetate may be readily calculated from the gram molecular value, which is 16,800 calories. The critical energy  $E_c$  is:

$$\frac{16,800 \times 4.2 \times 10^7}{6.06 \times 10^{23}} = 1.03 \times 10^{-12} \text{ erg}$$

The energy of one quantum  $h\nu$  which, according to Einstein's theory,<sup>70</sup> is necessary for a molecule to react "photochemically" should be equal to  $0.262 \times 10^{-12}$  erg. Thus, the critical increment  $E$  per molecule is of the order of about 4 quanta, a quantity obviously of the same order as the extra

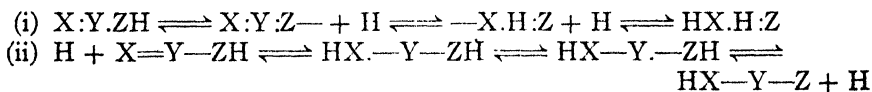
amount of energy required to be added to decompose one molecule of methyl acetate.

The mechanism suggested postulates that ions moving more slowly give rise to smaller frequencies, and therefore in the case of heavier ions the velocity, and consequently the vibration frequency, decrease and the quanta are less than those corresponding to the hydrogen ion. It is believed that no catalytic effects were observed, therefore, with potassium and lithium chlorides in the hydrolysis of methyl acetate.

While Marcelin did not make clear whether the presence or absence of a catalyst should affect the value  $E$ , Lewis found that the temperature coefficient of a reaction is independent of the quantity of catalyst present and that so far as the temperature coefficient of the reaction velocity is concerned, the mechanism of the action resulting in an increase in the internal energy may be accounted for by radiation.

The Arrhenius viewpoint that the catalytic effect of acids and bases consists in a direct kinetic influence of the hydrogen and hydroxyl ions has been modified by Lapworth.<sup>143, 144, 180</sup> Recognizing that the hydrogen ion in aqueous solution exists as a hydrate, and assuming an equilibrium between the hydrate and the free ion, he ascribed the catalytic effect exclusively to the latter. But the free hydrogen ion is identical with the hydrogen nucleus; due to its enormous heat of hydration, it cannot exist in solution and therefore may exert only a negligible kinetic effect (Brönsted). Rice, in connection with this point of view, suggested the existence of another modification of the free hydrogen ion possessing a much smaller heat of hydration than the ordinary hydrogen ion.

Brühl's theory<sup>43</sup> that ionization of an enol and the formation of a non-ionizable ketone by recombination of ions is the explanation for the keto-enolic change in ionizing solvents was found untenable, since it postulated a non-reversible change of enol into ketone. However, this theory led Lapworth<sup>142</sup> to adopt the viewpoint that an internal change takes place only in the ion of the reacting organic compound and that the function of the catalyst is to promote the formation of these ions. The catalytic activity of an acid was attributed to the formation of a reactive cation by the reversible addition of a hydrogen ion to the organic compound. The catalytic action of a base was due to the formation of a reactive anion by reversible removal of a hydrogen ion. The reversible removal of  $H'$  by a basic catalyst (i) and the reversible addition of  $H'$  by an acid catalyst (ii) Lapworth expressed in the following two schemes:



In these schemes no electrical charges are shown, but the spare bond in scheme (i) can be replaced by a negative charge, which is neutralized when  $H'$  is re-attached to the organic radical; the dot used in scheme (ii) to indicate the direction in which the "free affinity" of  $Y$  is temporarily disposed can be replaced by the opposite charges of an electrovalence. The internal change in (i) is a molecular rearrangement of the anion

$X:Y:\bar{Z} \rightleftharpoons \bar{X}:Y:Z$ , and in (ii) it is the formation of a double bond by the removal of a proton from one of two alternative positions in the cation  $HX.\dot{Y}.ZH \rightleftharpoons HX.Y:Z$ , or  $X:Y.ZH$ . The theory proposed by Lapworth<sup>142</sup> has been revived by Euler and his school, as well as by Kuhn and Jacob.<sup>139</sup>

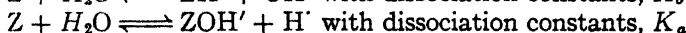
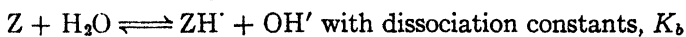
The assumption of intermediate compound formation between the reacting substances (the substrate) and the catalyst has often been used for qualitative explanation of catalytic processes. Euler<sup>71, 72, 73, 74</sup> conceived the idea that catalysis consists in the introduction of molecules by means of which the reaction proceeds through the formation of intermediate compounds. The reaction intermediates are ions of the substrate—a weak electrolyte, the catalyst—hydrogen ions, hydroxyl ions, or salts. The catalyst functions by increasing the concentration of the intermediates and also the mobility of the system. The intermediate step in the process is the formation of a salt between the catalyst and the substrate. Euler and Laurin<sup>76</sup> and Euler, Oländer and Rudberg<sup>80</sup> collected experimental evidence by studying hydrolytic reactions pointing to the fact that the hydrolyzable substrates catalyzed by acids, as well as by bases, must be amphoteric electrolytes, able to combine with both kinds of catalyst. Acids and bases when catalyzing hydrolytic reactions form compounds of the type of salts, when the catalyst is added to that group of the substrate in which hydrolysis is going to take place. It was the belief of Euler that an electric charge gives to these groups of atoms a tendency to split, and that in this charged or ionic state the substrate is more reactive. Euler postulated that the total reactivity of the substrate is expressed by the product of concentrations, while the specific reactivity is given by the presence of at least three kinds of molecules: (1) the free substrate molecules; (2) the substrate anions; and (3) the substrate cations. The theory of "interacting ions" proposed by Euler expresses the reaction velocity of catalytically accelerated hydrolytic conversion of glucose as follows:

$$K = K_0 + rq_1 \frac{K_a}{h} + rq_2 \frac{K_b}{K_w} \cdot h$$

$$1 + \frac{K_a}{h} + \frac{K_b}{K_w} \cdot h$$

$$h = \sqrt{\frac{K_a}{K_b} \cdot K_w}$$

where  $K_a$  and  $K_b$  are dissociation constants;  $K_0$ , reactivity of free glucose = 0.0012;  $rq$ , specific reactivity of glucose ions;  $h$ , minimum reaction velocity at the isoelectric point;  $rq_1$ , specific reactivity of glucose anions, and  $rq_2$ , specific reactivity of glucose cations. Glucose, supposed to be an amphoteric weak electrolyte, dissociates as follows:



Thus the velocity constant of a catalyzed reaction is determined by two values, namely,  $K$  and  $rq$  or, if the considered substrate is amphoteric, then by two pairs of constants,  $K_a$  and  $K_b$ — $rq_1$  and  $rq_2$ .

As a confirmation of the theory that catalysts active in homogeneous solutions, such as acids or bases, accelerate mutarotation of glucose to the extent to which they increase the concentration of the reaction intermitting ions of the substrate, it was shown<sup>77, 78</sup> that the experimentally determined activity—pH curve—stands in a complete agreement with the formula derived theoretically:

$$K_1 + K_2 = K_o + r q_2 \cdot \frac{K_b}{K_w} [H^+] + r q_1 \cdot \frac{K_a}{[H^+]}$$

While Euler and Oländer<sup>77, 78</sup> found the relationship between the constants  $K$  for the hydrolysis of benzamide and ethyl acetate and pH, Oländer<sup>79</sup> proved a minimum for saponification of esters and sulfonic acid esters. He found that the minimum or "isocatalytic point" happens to be at

$$h = \sqrt{\frac{K_a K_w}{K_b}}$$

when both kinds of ions are assumed to have equal reactivities. Euler assumed that it would be possible to predict the catalysts and catalytic velocities by applying the above reasoning. Knowing, for example, the constant  $K_a$  for dextrose and its isocatalytic point, the basic constant  $K_b$  could be found ( $10^{-19}$ ) and using this the dependence of rate of hydrolysis on pH could be established. Mutarotation is catalyzed through acids and bases. In acid catalysis, the reaction velocity is proportional to the concentration of the strong catalyzing acid as well as to the concentration of the H ions, while in the catalysis of bases, it is proportional to the concentration of the strong base as well as to the concentration of the OH ions. Between these two maxima lies the minimum of the reaction velocity. The position of this minimum and its absolute reaction velocity is influenced particularly through phosphates.<sup>75, 139</sup>

Kuhn and Jacob,<sup>139</sup> in studying mutarotation and inversion, found that the pH curve for inversion is asymmetric about the isocatalytic point, ascribing a specific reactivity to the anion 2.1 times that of the cation. Thus the isocatalytic point did not coincide with the isoelectric point and was expressed by a new formula in which it is referred to the specific reactivity of the ions  $K_a$  and  $K_b$ .

$$h = \sqrt{\frac{K_a}{K_b} \cdot K_w} \cdot \frac{K_a}{K_b}$$

The newly introduced factor gives  $K_b = 7.8 \cdot 10^{-17}$  a greater value than that previously obtained from the isocatalytic point.

Euler's theory of interacting ions is similar to the point of view of Marcelin, Brönsted, and others, as it assumes that acid and base catalysis is the result of collisions between molecules of the catalyst and the substrate. For the "critical complex" originating on this collision, no equilibrium is postulated.

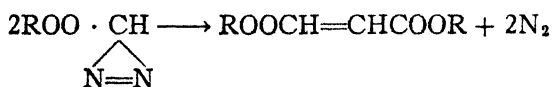
For the interacting ions, Euler and co-workers assume the existence of a definite average life span and therefore even a definite concentration. This has been illustrated in the hydrolysis of acetamide in which the ion  $\text{CH}_3\text{CONH}_2^+$ , or its corresponding hydrate  $\text{CH}_3\text{CONH}_2^+ \cdot \text{H}_2\text{O}$ , does

exist in measurable concentrations in solutions of a definite acidity. After a certain period, the valency electron of the group  $-\text{CONH}_3^+$  assumes labile positions so that the splitting of the molecule may take place. Only in a special case (the reactivity of the anion) when the splitting velocity  $\nu$  of the interacting ion is as large as its formation velocity the theory of "collision catalysis" and that of interacting ions may correspond to identical conceptions on acid and base catalysis.

The concept that only free ions participate in chemical reactions and that the reaction ability of a given solution is proportional to the number of free ions contained in it was not found to hold in all cases of acid and base catalysis. The alternative view, that the undissociated molecules of an acid or a base may have a catalytic action apart from that of the ions was first clearly emphasized by Acree,<sup>1</sup> Snethlage,<sup>194, 195</sup> Dawson and co-workers<sup>60</sup> and by Taylor,<sup>206</sup> who obtained for the ratio of catalytic activity of the molecule of the acid to that of its ions the value of 0.06 for picric acid and about 2.00 for hydrochloric acid. The co-action of  $\text{H}^+$  or  $\text{OH}^-$  and undissociated molecules constitutes the dual theory of homogeneous catalysis in solutions. The dual nature of acids and bases in catalysis has been advocated by Dawson and his co-workers.<sup>60</sup> They established the specific catalytic actions of  $\text{H}^+$  ions and undissociated acids in reactions, such as enolization, followed by the iodination of acetone and the hydrolysis of ethyl acetate.

The dual theory is based on the fact that the addition of neutral salts to a solution in which a reaction proceeds under the influence of acids or bases usually causes a marked acceleration. A classical example of this type of reaction is furnished by Arrhenius in the inversion of cane sugar in the presence of acetic acid when the addition of 0.1 M sodium chloride increased the velocity about 30 per cent. Brönsted, criticizing the dual theory, stated that two factors were overlooked in its development, namely, (1) the medium effect: the velocity constant of a reaction is not the same in pure water and in a tenth molar salt solution; and (2) the fact that, according to the modern theory of solutions, the mass action law cannot be applied in its classical form for calculating ionic concentrations, because then the effect due to undissociated acids would be foreshadowed. In other words, according to Brönsted, experimental facts on which the dual theory is based were misinterpreted.

Acids and bases appeared as strong catalysts in reactions taking place in solvents in which, due to the absence of electrolytic dissociation, no ions were formed. In indifferent solvents, such as tetrachlorethane, toluene, and other hydrocarbons in which no electrolytic dissociation of acids is possible, Hantzsch<sup>108</sup> sought a proof for the catalytic action of undissociated acids, hydrochloric acid and hydrobromic acid in the formation of fumaric acid ester from diazo acetic ester:



Hantzsch studied also the cane sugar inversion and diazo acetic ester

hydrolysis in aqueous solutions of strong acids and his optical findings indicated that the strength of acids not only was connected with their degree of dissociation, but seemed to be a function of the presence of undissociated molecules and their properties.

Lowry and Smith<sup>181</sup> and Lowry and Faulkner<sup>180</sup> collected many examples of the strong influence of acid and base molecules upon the reaction of mutarotation of glucose. The theory that H and OH ions are the sole catalysts in classical reactions, such as inversion of cane sugar and ester hydrolysis, and that the reaction velocity is proportional to their concentration, has been proved inadequate. The use of activities in place of concentrations, as well as the dual theory in first approximation, has failed to interpret all cases of acid and base catalysis. After an attempt was made to establish the effect of undissociated molecules exercising a catalytic influence, the participation of ions other than H<sup>+</sup> and OH<sup>-</sup> in catalytic action has been suggested, although it is implied that the specific activity of H<sup>+</sup> and OH<sup>-</sup> is considerably higher. Anion and cation catalysis has been differentiated. A typical example of anion catalysis is the mutarotation of glucose catalyzed to a great extent by acid anions, such as the acetate ion. Normally, this reaction proceeds with marked velocity only in alkaline media but, in the presence of sodium acetate, it may be accelerated even in weak acetic acid.<sup>32, 149</sup> On the other hand, the mutarotation of glucose may be influenced catalytically not only by H ions, but also by other cations.<sup>37</sup>

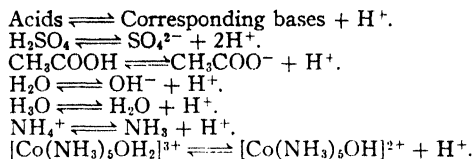
In the decomposition of nitramides (H<sub>2</sub>NNO<sub>2</sub>) by water and nitrous oxide, water is a weak catalyst, but the hydroxy-ions of cobalt amines, for example, [Co(NH<sub>3</sub>)<sub>5</sub>OH]<sup>2+</sup>, or basic molecules, such as aniline or other amines, act as strong catalysts.<sup>40</sup> The fact that many kinds of molecules and ions in the reaction system may function as catalysts in homogeneous liquid catalysis led Dawson and Brönsted to call their theory the "multiple theory." The theories on acid and base catalysis in homogeneous liquid systems outlined were succeeded by an "electrolytic" theory of catalysis advanced by Lowry<sup>149</sup> and Brönsted.<sup>32</sup> According to H. A. Lorentz, "All the transformations of matter including chemical reactions are essentially electric phenomena." It was the idea of de la Rive and later of Armstrong that in order to bring about a chemical reaction it is essential to use a system similar to a galvanic chain. These concepts led to a new definition of an acid as a substance which gives up a proton to a base, and of a base as a substance which accepts a proton from an acid. This point of view is convenient for the interpretation of the catalytic action not only of ions, but of undissociated molecules as well. Any acid or base compound answering the general criterion of the theory of splitting off or adding to a proton is considered suitable as a catalytic agent for acid or base catalyses.

Schwab,<sup>187</sup> in his book gives a table indicating that anions, as well as uncharged molecules, insofar as they possess protons able to be split off, may function catalytically as acids and, likewise, cations and uncharged molecules may act as base catalysts if they are able to take up protons. Water has a dual nature. Due to the ability to give off an H<sup>+</sup> ion according to the scheme:  $\text{H}_2\text{O} \longrightarrow \text{H}^+ + \text{OH}^-$  it functions as an acid; on the other

hand, by taking up an  $H^+$  ion according to:  $H_2O + H^+ \longrightarrow H_3O^+$ , it acts as a base.<sup>178, 219</sup>

Table 13.

(Schwab)



Lowry pictures the mechanism of catalysis according to the electrolytic theory in a manner that the proton-donor attaches itself to one of the points of attack of the molecule undergoing changes and immediately thereafter the proton-acceptor attaches itself to the other, whereby an electric current in the form of migrating valency electrons flows through the molecule from one to the other point of attachment. The rapidity with which these events follow upon one another is the reason of the short life of intermediate compounds. Brönsted recognizes that the net action to which the reacting components are subjected is either the acceptance or loss of a proton or its transference from one position in the molecule to another. Schwab emphasizes the possibility of three primary reactions in case of an acid catalysis:

- (1)  $HZ + H^+ \longrightarrow HZH$  (collision complex formation<sup>156, 157</sup> Brönsted).
- (2)  $HZ + H^+ \rightleftharpoons HZH^+$  (equilibrium intermediate substance according to Bjerrum; Arrhenius intermediate substance).
- (3)  $HZ + H_2O \longrightarrow HZH^+ + OH^-$  (formation of reaction mediating ions according to Euler<sup>72, 73, 79, 81</sup>).

where  $HZ$  denotes the reacting molecules stable in themselves;  $HZH^+$ , formation in acid catalysis—a rearrangement accompanied by chemical conversion due to the giving off of a proton, and  $Z$ , formation in base catalysis.

The empirical equation by Brönsted:  $K_c = GK_1x$  holds for reactions catalyzed by acids and bases, where  $K_c$  is a catalytic constant of a given acid or base;  $K_1$ , its electrolytic dissociation constant, and  $G$  and  $x$ , constants at a given temperature. In the attempt to give a theoretical base for this relationship, the kinetic expression for the reaction velocity  $K_c = PZe^{-E/RT}$  has to be considered, in which  $Z$  is the collision number  $P$ , the orientation factor, and  $E$ , the activation energy. The collision number  $Z$  and the orientation factor  $P$  may be assumed to be constant for a definite reacting substance and a series of similar catalysts. The activation energy  $E$  depends on the tendency of the catalyst to give off or take up a proton. The activation energy is either a kinetic energy originating on collision of both molecules, or a vibration energy of the proton which favors its transition on collision. In both cases a linear relationship with the dissociation energy has to be expected within a small interval.<sup>18, 19</sup>

From the electrolytic theory viewpoint, it seems to make little differ-



ence in the nucleus process whether in acid catalyses an undissociated acid molecule or a complex cation, such as a hydrogen ion solvated by the solvent, is added temporarily to the reacting molecules, or whether in a corresponding base catalysis an undissociated base, an acid anion, a hydroxyl ion, or another proton-acceptor causes the withdrawal of a proton from the reacting molecules. The catalytic behavior of various proton-donors and proton-acceptors is expressed in their specific catalytic action constants, reflecting the individual velocities with which the giving off and acquiring of protons takes place. The specific catalytic actions of complex ions formed from  $H^+$  ions and the solvent molecules often differ greatly. Complex ions in water are  $(H_3O)^+$ ; in alcohol  $(C_2H_5OH_2)^+$ . In a mixed solvent, for example, water containing alcohol, an equilibrium is established between the complex ions, and a small shift in it may strongly influence the reaction course. Complexes formed from  $H^+$  ions and alcohol molecules, such as  $ROH_2^+$ , may be catalytically more active than those complexes formed from  $H^+$  ion and  $H_2O$ , namely  $HOH_2^+$ . From this point of view, Goldschmidt<sup>100, 101</sup> attempted to explain the inhibition exercised by water upon acid catalysis in esterification reactions in alcoholic solutions.

On the basis of the chemical equilibrium, known as the acid-base equilibrium, and defining an acid and a base, namely,



an acid is a proton-donor, a base a proton-acceptor, and an ampholyte is both proton-donor and proton-acceptor. According to these conceptions, Lowry classified solvents into three groups:

(a) Solvents which are either acids or bases are not catalysts, but may function in the presence of auxiliary catalysts.

(b) Solvents which are neither acids nor bases are completely inactive.

(c) Amphoteric solvents which act as true catalysts.

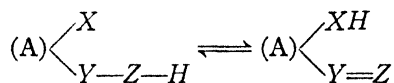
Upon certain conversions in solutions the catalytic influence is exercised not only by inorganic acid and basic compounds or by the inorganic ingredients, such as  $H$  or  $OH$  ions set free on electrolytic dissociation of organic acids and organic bases, but by the undissociated organic molecules themselves, as well as by their organic dissociation products, such as the organic cations of bases and organic anions of acids. In the formation of anilides from organic acids and aniline, picric acid acts as a strong catalyst. It is believed that aniline picrate originates intermediately which, through exchange with the organic acid, gives anilide.<sup>102, 103</sup> Goldschmidt considered the aniline salt of picric acid and not its anion or cation as the active catalyst in the formation of anilide, because the aniline salt in aniline solution has a relatively small dissociation ability, and the reaction velocity in the presence of picric acid alone is proportional to its concentration. Bredig,<sup>30</sup> Braune,<sup>29</sup> and Snethlage<sup>194, 195</sup> ascertained the catalytic action of organic acids in an undissociated state in the decomposition of diazoacetic acid ester. On the other hand, the decomposition of:  $H_2N_2O_2 \longrightarrow N_2O + H_2O$  has been strongly accelerated not through  $OH^-$  ions, but, as revealed by the kinetic study, through the exclusive action of undissociated base molecules.<sup>35, 36, 40, 42</sup> It has been stated also<sup>129</sup> that the bivalent cation of

a complex cobalt salt may accelerate the decomposition of nitramide molecules such as, for example, the  $[\text{Co}(\text{NH}_2\text{OH})_6]^{2+}$  which with  $\text{H}^+$  ion is converted into the catalytically active cation,  $[\text{Co}(\text{NH}_2\text{OH})_6]^{3+}$ .

Attempts have been made to ascertain the reasons for, as well as to determine the kinds of rearrangements taking place in the different types of acid and base catalysis in homogeneous systems. The "proton" theory in its general form recognizes that an intramolecular electrolysis sets in instantaneously with the splitting off or the addition of a proton. As a result of an electronic displacement caused by an acid catalyst throughout the atoms of the reacting molecules, the shift of valence electrons affects the migration of double bonds and positive polarization of a previously non-polar bound H atom, whereby the latter is taken up by the proton-acceptor—the base (Lowry). The reverse takes place in base catalysis in which a proton is split off by rapid electron displacements, resulting in a migration of valence electrons, displacement of double bonds, and the formation of a negative charge on a molecule other than the one originally rendered negative. The newly formed negative charge is neutralized by the proton liberated by the acid, and the rearrangement of the reacting molecules is brought about finally through the incorporation of the proton in a homopolar bond.

As has been previously mentioned, acid and base catalysis in homogeneous systems may be subdivided into those reactions which are: (1) catalyzed exclusively by acids, such as the hydrolytic splitting of mono-, di-, and polysaccharides, dextrans, starches, and esters, as well as the decomposition of ethers and ether-like compounds, also alkylacetates, glucosides, etc. (refer to Table 14); (2) catalyzed exclusively by bases, such as the decomposition of nitramides, the isomerization of nitromethane, various auto-racemizations, and the saponification of many mineral acid esters, carbonic acid ester,  $\beta$ -lactone, diacetone alcohol, etc. (refer to Table 15); and (3) catalyzed by both acids and bases, such as the saponification of esters, lactic acid and lactide, the hydrolysis of acid amides, the hydration of carbonic acid anhydride, the enolization of acetone, and the mutarotation of various sugars; in other words, protropic isomerizations, etc. (refer to Table 16).

The prototropic reaction systems furnish the best examples of molecular rearrangements. Mutarotation of glucose or enolization of acetone are examples of prototropic isomerization in which internal rearrangements are recognized through place exchange of a proton within the reacting molecules. If  $X$ ,  $Y$ ,  $Z$  are optionally O, N, or C atoms, then the enolization may be expressed:  $\text{H}-\text{X}-\text{Y}=\text{Z} \rightleftharpoons \text{X}=\text{Y}-\text{Z}-\text{H}$ , and the mutarotation:



The H or proton migration in its turn causes the displacement or change in valency, thus affecting the binding rates within the reacting molecule. From the standpoint of the electronic displacement theory, Lowry describes

(Text continued on page 200)

Table 14. Acid Catalysis.

Catalytic.	Reaction	Catalyst	Observer
		Concentrated acids.	Deiman (1795).
	Hydration of acid anhydrides.	Formic, acetic and oxalic acids.	Mischlaschewsky: <i>Ber.</i> , <b>24</b> , (1891).
	Hydration of acetylene to acetaldehyde.	H <sub>2</sub> SO <sub>4</sub> and Hg salts.	Neumann and Schneider: <i>Z. angew. Chem.</i> , <b>33</b> , 189 (1920); <i>J. Am. Chem. Soc.</i> , <b>45</b> , 1552 (1923).
	Dehydration of alcohols (without a solvent) by heating to form unsaturated hydrocarbons.	Small amount of concentrated H <sub>2</sub> SO <sub>4</sub> . H <sub>3</sub> PO <sub>4</sub> . Formic acid.  Water-free oxalic acid.	de Foureroy and Vanguelin (1797). Mitscherlich (1833). Newth: <i>J. Chem. Soc.</i> , <b>79</b> , 915 (1901). Wallach: <i>Ann.</i> , <b>291</b> , 361 (1896); <b>356</b> , 243 (1907). Zelinsky and Zelikow: <i>Ber.</i> , <b>34</b> , 3250 (1907); <i>Ann.</i> , <b>31</b> , 63 (1839).
	Inversion of cane sugar (splitting of cane sugar into glucose and fructose).	Acids.	Ostwald, W.: <i>J. prakt. Chem.</i> (2), <b>29</b> , 401 (1884); (B), <b>39</b> , 1756 (1906). Caldwell: <i>Brit. Assoc. Advancement Sci. Rep.</i> , 351 (1906). Haworth and Law: <i>J. Chem. Soc.</i> , <b>109</b> , 1314 (1916). Haworth and Limell: <i>J. Chem. Soc.</i> , <b>123</b> , 294 (1923). Pennychick: <i>J. Chem. Soc.</i> , <b>125</b> , 2049 (1924); <i>J. Am. Chem. Soc.</i> , <b>48</b> , 6 (1926). Scatchard: <i>Ibid.</i> , <b>43</b> , 2406 (1926). Jones and Lewis: <i>J. Chem. Soc.</i> , <b>117</b> , 1120 (1920). Fales and Morrell: <i>J. Am. Chem. Soc.</i> , <b>43</b> , 2071 (1922).
	Inversion of cane sugar.	Weak acids added to small concentrations of strong acids increase the velocity (10% per unit of the concentration of the weak acid).	Arrhenius: <i>Z. physik. Chem.</i> , <b>4</b> , 22 (1889).
	Ester hydrolysis.	Different acids.	Ostwald, W.: <i>Z. physik. Chem.</i> , <b>1</b> , 78 (1887).
	Hydrolysis of ethers and ether-like compounds, such as alkyl acetal (the disaccharides—inversion of sugar).	Acids.	Ostwald, W.: <i>J. prakt. Chem.</i> (2), <b>29</b> , 385 (1884).
	Hydrolysis of ethers in the gas phase; T. about 400°; to recovery of alcohol.	ThO <sub>2</sub> .	Sabatier and Espil: <i>Bull. soc. chim.</i> , <b>15</b> , 228 (1914).
	Hydrolysis of esters in the gas phase; ester vapor with excess of water vapor led over the catalyst at 300° to aqueous acid and alcohol; the saponification of esters serves to obtain pure conc. acids, e.g., acetic acid methyl ester is led with water (necessary amount) over the catalyst; T. 180–220°; the reaction proceeds as follows: $2\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} = \text{CH}_3\text{OCH}_3 + 2\text{CH}_3\text{COOH}.$ In addition to small amount undecomposed ester, the outlet gases contain glacial acetic acid and dimethyl ether.	TiO <sub>2</sub> or ThO <sub>2</sub> .  Cu container charged with H <sub>2</sub> SO <sub>4</sub> or H <sub>3</sub> PO <sub>4</sub> .	British Celanese, Ltd.: E. P. 284, 582 (1928).

Table 14 (Continued).

Reaction	Catalyst	Observer
Racemizing of phenylmethylacetophenone and phenylisobutyl acetophenone in various solvents; phenylmethylacetophenone in $C_6H_5Cl$ at $99.4^\circ$ ; phenylisobutylacetophenone in the presence of dichloroacetic acid in anisol, nitrobenzene, chlorbenzene and Decalin at $100^\circ$ ; the reaction mechanism postulates formation of a hybriide:	Mono-, di-, trichloroacetic acid and <i>o</i> -nitrobenzoic acid.	Bell, Lietwell and Wright: <i>J. Chem. Soc.</i> , 1938, 1861-65.
$>CH \cdot CO- + HA \rightleftharpoons \left\{ \begin{array}{l} CH \cdot C(OH)- \\ CH^+ : C(OH)- \end{array} \right\} + A^-$ <div style="display: flex; justify-content: space-around; width: 100%;"> <span>hybriide</span> <span>anion</span> </div>		
The step determining the velocity following thereafter consists in giving off a proton and racemizing; racemizing in the absence of acids is catalyzed through triethylamine in $C_6H_5Cl$ .		
Hydrolysis of cellulose.	$H_2SO_4$ .	Braconnet: <i>Ann. chim.</i> , 12, 172 (1819). Ost, H., Wilkening and Brodtkorb: <i>Chem.-Ztg.</i> , 34, 461 (1910); 35, 1125 (1911). Bechamp: <i>Compt. rend.</i> , 42, 1210 (1856).
Hydrolysis of cellulose; yield, 95% of glucose splitting readily on heating.	HCl.	Willstätter and Zechmeister: <i>Ber.</i> , 43, 23 (1914).
Hydrolysis of cellulose; small pieces of wood dried up to 0.5% $H_2O$ content are charged with HCl-sugar solution, the remaining cellulose being treated for 8 hrs. with 40% HCl; yield, 28% glucose and 26% HCl; the HCl-sugar solution is evaporated in vacuum or treated by heating and spraying in petroleum oil; yield conc. solution with 60% sugar neutralized with lime.	HCl-sugar solution 40% HCl.	Rheinau process accorded to Willstätter and Hägglund.
Hydrolysis of cellulose; optimum T. $30^\circ$ .	HCl acid; HCl gas.	Hägglund: G.P. 367,230 (1922). G.P. 378,989 (1922). G.P. 382,463 (1923). (Levy-Koch process).
Hydrolysis of cellulose; wood splinters are not dried, but treated in a tunnel oven in an opposite stream with HCl; the mass having adsorbed 6% HCl acid is treated with 40% HCl; a gradual conversion of cellulose to sugar takes place.	40% HCl.	Prodor Gesellschaft in Genf (Terisse and Levy): (Prodor process) Bergius: <i>Z. angew. Chem.</i> , 41, 707 (1928).
Hydrolysis of starch (sugar formation).	Mineral acids.	Parmentier: (1781). Dobreriner: (1808). Kirchhoff: (1811).
Hydrolysis of starch to (1) dextrans and (2) starch sugars; T. $170-200^\circ$ ;	0.2-0.4% strong $HNO_3$ HCl, $HSO_3$ or oxalic acids.	
(1) the roasted dextrans contain 8% $H_2O$ , 5% dextrose, 0.5% ash and 85% dextrin;	0.5-0.8% HCl.	
(2) starch sugars; starch milk, $21^\circ$ Bé, vapor is passed under pressure 1-1.5 atm. until the solution shows the erythro-dextrin reaction with $I_2$ -KI solution; 50% of initial starch converted into dextrose and dextrin under stirring, neutralized with lime or soda, filtered under pressure and decolorized with bone coal; concentrated by vacuum evaporation to $42-44^\circ$ Bé.		

Table 14 (Continued).

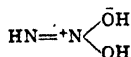
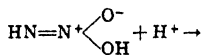
Reaction	Catalyst	Observer
Hydrolytic splitting of disaccharides and polysaccharides, such as maltose, lactose, dextrose, starch.	Aqueous solutions of acids.	Noyes and Hall: <i>Z. physik. Chem.</i> , <b>18</b> , 240 (1895).
Ester hydrolysis $\begin{array}{c} \text{H}-\text{C}-\text{COO} \cdot \text{C}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \\ \diagup \\ \text{N}=\text{N} \end{array}$ $\text{HO}-\text{CH}_2-\text{COO} \cdot \text{C}_2\text{H}_5 + \text{N}_2$	Acids (H ions).	Fränkel: <i>Z. physik. Chem.</i> , <b>60</b> , 202 (1907).
Hydrolysis of <i>o</i> -acetic acid esters to acetic ester; the <i>o</i> -carbonic acid ester to carbonic acid ester.	Acids.	Scrabal and Baltadschiewa: <i>Monatsh.</i> , <b>45</b> , 19, 95 (1924).
Autocatalyzed ester hydrolysis.	Acids.	Dawson and Lawson: <i>J. Chem. Soc.</i> , <b>1928</b> , 3218-27.
Hydrolysis of ethyl acetate.	Monochloroacetic acid.	Dawson and Lawson: <i>J. Chem. Soc.</i> , <b>1929</b> , 393-401.
Hydrolysis of ethyl acetate at 25°.	HCl, HNO <sub>3</sub> , HClO <sub>4</sub> , chloroacetic acid, glycolic acid and acetic acid.	Dawson and Lawson: <i>Proc. Leeds Phil. Lit. Soc. Sci. Sect.</i> , <b>2</b> , 331-35 (1932); refer also to Dawson and Powis: <i>J. Chem. Soc.</i> , <b>103</b> , 2135-46 (1912). Dawson and Cram: <i>J. Chem. Soc.</i> , <b>109</b> , 1262-77 (1916).
Ammonolysis of malonic acid ester in liquid ammonia.	Malonic amide and alcohol, both end products, act as acids in liquid ammonia; NaCl, NaBr, and NaI also increase catalytic activity; likewise equivalent amounts of various ammonium salts give equal effect.	Slobutsky and Audrieth: <i>Trans. Ill. State Acad. Sci.</i> , <b>29</b> , 104-105 (1936).
Acid catalysis in liquid ammonia; ammonolysis of ethyl benzoate to form benzamide; T. 0-25°; the catalytic action is almost proportional to the concentration of the salt.	Ammonium salts acting as acids (proton donors); NH <sub>4</sub> Cl, NH <sub>4</sub> Br, HN <sub>4</sub> ClO <sub>4</sub> , C <sub>6</sub> H <sub>5</sub> CONH <sub>4</sub> ; the increase in the activity of the catalyst series is reversed by an increase in the degree of dissociation.	Fellinger and Audrieth: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 579-581 (1938).
Hydrolysis of phosphonformic acid according to the equation: $\text{HOOC} \cdot \text{PO}(\text{OH})_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 + \text{HPO}(\text{OH})_2$	The free acid, as well as the primary anion undergoes spontaneous hydrolysis influenced by the medium and catalyzed by the H <sup>+</sup> ions; (for high concentration of H <sup>+</sup> ions, a decrease in the catalytic effect of H ions takes place).	Nylén: <i>Z. anorg. allgem. Chem.</i> , <b>235</b> , 33-41 (1937).
Ammonolysis of santonin in liquid ammonia.	Weak acid, such as glucose, increases considerably the velocity; acetamide, urea, carbazol, benzamide, phenolformamide, NH <sub>4</sub> acetate, NH <sub>4</sub> formate, CH <sub>3</sub> CHCOONH <sub>4</sub> , and C <sub>6</sub> H <sub>5</sub> COONH <sub>4</sub> ; introduction of CN group does not increase catalytic activity of the carbonic acids, but introduction of CN into the acid amide increases catalytic action; substitution of the methyl group through the phenyl increases the catalytic activity.	Schattenstein: <i>Zhur. Fiz. Khimii</i> , <b>8</b> , 613-18 (1936).

Table 14 (Continued).

Reaction	Catalyst	Observer
Alcoholysis of diazoacetic ethyl ester.	Trinitrobenzoic acid, trichloroacetic acid, picric acid, sulfosalicylic acid, trichlorobutyric acid.	Millar: <i>Z. physik. Chem.</i> , <b>85</b> , 129 (1913). Bredig: <i>Z. Elektr.</i> , <b>18</b> , 535 (1912).
Esterification of benzoic or phenylacetic acid.	HCl, HBr, picric acid.	Goldschmidt: <i>Ber.</i> , <b>28</b> , 3218 (1895).
Esterification of phenylacetic and acetic acid in alcoholic solution.	The more strongly dissociated acid is a better catalyst.	Goldschmidt and Sunde: <i>Ber.</i> , <b>39</b> , 711 (1906). Goldschmidt: <i>Z. Elektr.</i> , <b>15</b> , 4 (1909).
Ester formation.	Complex ions originating by the addition of H ions to a neutral molecule.	Müller: <i>Z. physik. Chem.</i> , <b>134</b> , 190-92 (1928).
Esterification of formic acid.	Acids (H ions).	Goldschmidt, Haaland and Sommerschild-Melbye: <i>Z. physik. Chem. (A)</i> , <b>143</b> , 278 (1929).
Esterification of aliphatic acids (oxalic, succinic) to methyl ester; esterification of aliphatic acids gives better yields than esterification of aromatic acids (benzoic acid); from acetic acid are also obtained ethyl, isopropyl and glycol esters; in general, dimethyl esters are obtained from the dibasic acids; both the monomethyl and dimethyl esters are obtained from adipic acid; the organic acid (0.5-1.0 mol) is boiled in a 500 cc. flask with water-free alcohol in excess (3-6 mol) for 2-4 hours, using a reflux condenser; the reaction product is fractionated and the excess acid removed by washing with sodium bicarbonate solution and the ester extracted with ether.	Dihydroxyfluoboric acid.  1-2% Dihydrofluoboric acid.	Kroeger, Sowa and Nieuwland: <i>Proc. Indiana Acad. Sci.</i> , <b>46</b> , 115-117 (1937).
Esterification to form methyl acetate (suitable also for preparing propionic acid from carbon monoxide and propyl alcohol).	Catalyst prepared as follows: 3 mols anhydrous liquid HF are converted with 1/2 mol metaboric acid or with 1 mol boric acid (or 1643 parts HF with 1696 parts boric acid) at -92 to 200°; likewise to 1500 parts of compound from HF and boric acid may be added 417 parts anhydrous BF <sub>3</sub> below 10°; in these reactions, hydrates of the formula BF <sub>3</sub> · 2H <sub>2</sub> O or BF <sub>3</sub> · 3H <sub>2</sub> O are formed.	Dupont (McAlevy): U.S.P. 2,135,454, Nov. 1, 1938.
Esterification of ethyl alcohol to ethyl acetate (small amount of acetic acid); T. 275°; yield, 37-54%.	Cr oxide and freshly precipitated Al hydroxide; Cu with 10% Al <sub>2</sub> O <sub>3</sub> and 2% Cr <sub>2</sub> O <sub>3</sub> is likewise active and stable; similar is the activity of catalysts activated with rare earths (0.2% Ce or 0.9% Zr).	Lettschuk, Weltisstowa and Borisowa: <i>Zhur. Priklad. Khim.</i> , <b>11</b> , 56-60 (1938).
Re-esterification of <i>d</i> -bornyl-, benzyl-, $\alpha$ -phenethyl-, $\beta$ -phenethyl-, benzhydriyl- and cyclohexyl acetate with methanol; 100 mol methanol per 1 mol ester; 5 hours heating to 200° in sealed Duran glass tubes.	Pt, Cu, Ni, German silver, brass, cast iron, malleable iron, ordinary steel, acid-resistant steel.	Berker and Hjulstad: <i>Ber.</i> , <b>71</b> , 2052-2056 (1938).

Table 14 (Continued).

Reaction	Catalyst	Observer
Ether formation from alcohols.	Arsenic acid, as well as aromatic sulfonic acids.	Kraft and Roos: <i>Ber.</i> , <b>26</b> , 2829 (1893); G.P. 223,795.  Barbier and Grignard: <i>Bull. soc. chim.</i> (4), <b>3</b> , 139 (1908); <b>5</b> , 512 (1909). Shell Development Co. (Evans and Bullard): U.S.P. 2,067,385, Jan. 12, 1937.
Methyl-butyl ether from $C_4H_{10}$ — $C_4H_8$ mixture treated with $CH_3O$ (95–100%).	HCl, $H_2SO_4$ , $H_3PO_4$ .	Abel: <i>Z. Elektr.</i> , <b>18</b> , 545 (1912); <b>18</b> , 705 (1912). Abel and Bawm: <i>Monatsh.</i> , <b>34</b> , 425 (1912).
Catalysis of $H_2O_2$ .	Molybdc acid (half dissociated permolybdc acid molecule more efficient than the bivalent anion).	Livingston: <i>J. Am. Chem. Soc.</i> , <b>54</b> , 2393–94 (1932).
Decomposition of $H_2O_2$ in solutions of HBr and KBr compared with that in solutions of $H_2SO_4$ and KBr; a 10% increase in velocity.	Acid ions: $H_2SO_4$ .	Euler and Oländer: <i>Z. anorg. allgem. Chem.</i> , <b>147</b> , 295–311 (1925). Bredig: <i>Z. Elektr.</i> , <b>18</b> , 535 (1912). Braune: <i>Z. physik. Chem.</i> , <b>85</b> , 170 (1913). Snethlage: <i>Z. physik. Chem.</i> , <b>85</b> , 211 (1913); <i>Z. Elektr.</i> , <b>18</b> , 539 (1912). King and Bolinger: <i>J. Am. Chem. Soc.</i> , <b>58</b> , 1533–42 (1936).
Splitting of acetic acid.	Strong acids (bases).	
Decomposition of diazo acetic acid ester.	Organic acids.	
Decomposition of diazo acetate ions in aqueous solution leading to $N_2$ formation and glycolation (K diazoacetate is prepared by hydrolysis of diazo acetic ester with KOH).	Catalyzed strongly by H ions; the mol catalysis constant of ( $H_3O$ ) <sup>+</sup> is $3.57 \cdot 10^8$ , the highest value known for any reaction.	
Decomposition of ethyl diazoacetate; the reaction velocity constant $K$ is expressed with respect to ordinary ( $H$ ) in the organic medium (A) $K = K_H(H)$ ; the $K_H$ is found to decrease with the concentration of the catalyst ( $K_H = 39.0$ resp. 35.5 in 0.04 resp. 0.0005 mol. solution). $K_H$ varies more strongly with an acid-salt mixture as catalyst (39.9–33.3) (the strength of the used acid influences $K_H$ ).	Organic acids; activity of H determined by EK measurements.	Duboux: <i>Bull. soc. Vaad sci. natural</i> , <b>59</b> , 279–320 (1937). Refer also to MacInnes: <i>J. Am. Chem. Soc.</i> , <b>41</b> , 1086 (1919). Harned: <i>J. Am. Chem. Soc.</i> , <b>42</b> , 1808 (1920).
Inversion of saccharose T. 25°; (B) $K = K_H' \cdot A_H$ where $K_H$ and $K_H'$ are proportionality factors, depending on the catalyzed reaction, temperature and medium.	HCl or HCl-containing NaCl, $NH_4Cl$ , or $MgCl_2$ .	
Splitting off of nitrogen from diazo acetic acid ester (industrial process).	Acids.	Bredig and Fränkel: <i>Z. Elektr.</i> , <b>11</b> , 525 (1905). Bredig: <i>Verhandl. natur Med. Verein, Heidelberg</i> , <b>9</b> , 32 (1907). Bredig: <i>Z. Elektr.</i> , <b>18</b> , 535 (1912). Fränkel: <i>Z. physik. Chem.</i> , <b>60</b> , 202 (1907). Staudinger and Gaule: <i>Z. physik. Chem. (B)</i> , <b>49</b> , 1897 (1916). Braune: <i>Z. physik. Chem.</i> , <b>85</b> , 170 (1913).
Decomposition of nitramide; mechanism assumed:	HCl.	Marlies and La Mer: <i>J. Am. Chem. Soc.</i> , <b>57</b> , 1812–1820, 2739 (1935).



This compound is unstable and decomposes to  $N_2O$  and ozonium ion;  $K_{HCl} = +0.328 \cdot 10^{-7}$  (0–0.4 molar).

Table 14. (Continued).

Reaction	Catalyst	Observer
Decomposition of nitramide in <i>m</i> -cresol; the molecular catalysis constants increase with increase in the acid as well as the base concentration.		King and Bolinger: <i>J. Am. Chem. Soc.</i> , <b>58</b> , 1533-1542 (1936).
Decomposition of nitramide in aqueous solution; T. 15°, 25°, 35° and 45°.	Anions of trimethyl acetic acid, acetic acid, benzoic acid, formic acid, salicylic acid, monochloroacetic acid, <i>o</i> -nitrobenzoic acid, dichloroacetic acid.	Baughan and Bell: <i>Proc. Roy. Soc. London (A)</i> , <b>158</b> , 464-478 (1937).
Diazotation of aniline.	In Br ion catalysis the velocity constant 100 times greater than that of Cl ion catalysis, the slowing down action of H <sup>+</sup> is far-reaching, compensated.	Schmidt and Schubert: <i>Z. Elektr.</i> , <b>43</b> , 626-29 (1937).
Splitting off of carbonic acid from $\alpha$ -nitrocarbonic acids.	Acids.	Heuberger: <i>Svensk Kem. Tid.</i> , <b>38</b> , 340-378 (1926). Pedersen: <i>Trans. Far. Soc.</i> , <b>23</b> , 316 (1927).
Acetone-iodine reaction.	0.5 N acetic acid (the un-ionized acid is responsible for the catalytic effect); velocity increased twofold.	Goldschmidt: <i>Z. physik. Chem.</i> , <b>70</b> , 687 (1910). Goldschmidt: <i>Z. Elektr.</i> , <b>17</b> , 684 (1911). Bredig, Millar and Braune: <i>Ibid.</i> , <b>18</b> , 535 (1912). Snethlage: <i>Ibid.</i> , <b>18</b> , 539 (1912). Dawson and Powis: <i>J. Chem. Soc.</i> , <b>1913</b> , 2135.
Acid catalysts in non-aqueous media; inversion of <i>l</i> -menthon in chlorbenzene solution; T. $99.4 \pm 0.05^\circ$ ; a complex formation between <i>l</i> -menthon with the 3 chloroacetic acids: phenylpropionic acid, <i>m</i> -nitrobenzoic acid, benzoic and acetic acid in C <sub>6</sub> H <sub>5</sub> Cl which is assumed to be a protolytic reaction.	Mono-, di-, and trichloroacetic acid, <i>o</i> -nitrobenzoic acid, benzoic acid, and picric acid.	Bell and Caidin: <i>J. Chem. Soc.</i> , <b>1938</b> , 382-89.
Ketone splitting of $\alpha$ , $\alpha$ -dimethyl acetic acid in <i>o</i> -chloranilinium and anilinium, chloride buffer solutions.	H:	Pedersen: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 595-601 (1938).
Bromination of acetone enolization in light water and H <sub>2</sub> O—D <sub>2</sub> O mixture at 25°; the bromination velocity of acetone is equal to the exchange velocity for the first hydrogen atom.	H ions; enolization in D <sub>2</sub> O in the presence of D <sub>3</sub> O <sup>+</sup> ions is 2.1 times as rapid as in H <sub>2</sub> O in the presence of H <sub>3</sub> O <sup>+</sup> ; heavy acetone enolizes 7.7 times slower than light acetone.	Reitz: <i>Z. physik. Chem. (A)</i> , <b>179</b> , 119-34 (1937).
Bromination of <i>m</i> -nitroacetophenone, <i>o</i> -nitraniline and <i>p</i> -chlor- <i>o</i> -nitraniline.	Acetic acid-sulfuric acid mixtures.	Paul and Hammett: <i>J. Am. Chem. Soc.</i> , <b>58</b> , 2182-87 (1936).
Formation of anilides from organic acids and aniline.	Picric acid (through formation of aniline picrates).	Goldschmidt: <i>Z. physik. Chem.</i> , <b>24</b> , 353 (1898); <i>Ber.</i> , <b>39</b> , 97 (1906); <i>Z. physik. Chem.</i> , <b>70</b> , 642 (1910).
Conversion of acetyl chloramino benzene to <i>p</i> -chloroacetanilide.	Dilute HCl.	Acree and Johnson: <i>J. Am. Chem. Soc.</i> , <b>37</b> , 410 (1907); <b>38</b> , 258 (1907).
Conversion of creatine in creatinine in aqueous respectively alcoholic solutions.	Acids.	Edgar and Wakefield: <i>J. Am. Chem. Soc.</i> , <b>45</b> , 2242 (1923).
Conversion of <i>n</i> -iodine formanilide in anisole solution.	Acid catalysis in non-aqueous solvent.	Bell and Brown: <i>J. Chem. Soc.</i> , <b>1936</b> , 1520-24.



Table 15. Base Catalysis.

Reaction	Catalyst	Observer
Complex homogeneous catalysis of $\text{H}_2\text{O}_2$ by $\text{NaMoO}_4$ .	Small alkali concentration ( $\text{OH}^-$ ions) catalyze (in higher alkali conc. molybdate is catalytically inactive).	<i>Z. physik. Chem.</i> , <b>126</b> , 1-23 (1928).
Conversion of benzile in benzoic acid.	Aqueous $\text{NaOH}$ gives rates greater than those in pure water.	Klinger: <i>Ber.</i> , <b>19</b> , 1868 (1886). Nef: <i>Ann.</i> , <b>298</b> , 372 (1897). Lachman: <i>J. Am. Chem. Soc.</i> , <b>44</b> , 330 (1922); <b>45</b> , 1509 (1923); <b>46</b> , 779 (1924). Schening: <i>Ber.</i> , <b>56</b> , 253 (1923). Schoneberg and Keller: <i>Ber.</i> , <b>56</b> , 1638 (1923).
Disproportionating of two aromatic aldehyde molecules, especially benzaldehyde, to corresponding acids, benzoic acid and corresponding alcohol benzyl alcohol (Cannizzaro's reaction).	Alkalies.	Cannizzaro: <i>Ann.</i> , <b>88</b> , 129 (1853). Claisen: <i>Ber.</i> , <b>14</b> , 2475 (1881); <b>20</b> , 646 (1887). Kohn and Trauton: <i>J. Chem. Soc.</i> , <b>75</b> , 1155 (1899). Lachman: <i>J. Am. Chem. Soc.</i> , <b>45</b> , 2356 (1923). Geib: <i>Z. physik. Chem. (A)</i> , <b>169</b> , 41 (1934). Meerwein and Schmidt: <i>Ann.</i> , <b>444</b> , 221 (1925).
Saponification of mineral acid esters.	Bases.	Cavalier: <i>Ann. chim. phys.</i> , <b>18</b> , 449 (1899). Wegscheider and Furcht: <i>Monatsh.</i> , <b>23</b> , 1093 (1902). Wegscheider: <i>Ber.</i> , <b>41</b> , 52 (1902); <b>52</b> , 235 (1919). Kremann: <i>Monatsh.</i> , <b>28</b> , 13 (1907); <b>38</b> , 53 (1917). Seuter: <i>Chem. Soc. London (J. Chem. Soc.)</i> , <b>24</b> , 89 (1908); <i>J. Chem. Soc.</i> , <b>91</b> , 460 (1907). Klemene: <i>Monatsh.</i> , <b>38</b> , 553 (1917). Johansson and Sebelius: <i>Ber.</i> , <b>51</b> , 480 (1918). Olivier: <i>Rec. trav. chim.</i> , <b>41</b> , 303 (1922). Olivier and Berger: <i>Rec. trav. chim.</i> , <b>41</b> , 637 (1922).
Saponification of $\beta$ -lactone.	Base.	Johansson: <i>Hj. Lunds Univ. Arsskrift N. Acad.</i> , <b>12</b> , 2 (1916) (Nr. 8).
Saponification of carbonic acid ester.	Base.	Skrabal: <i>Monatsh.</i> , <b>38</b> , 305 (1917).
Decomposition of nitramides.	Negatively charged hydroxyl ion, acetate ion, neutral bases, such as aniline, amines; positively charged bases such as $[\text{Co}(\text{NH}_3)_5\text{OH}]^{++}$ .	Brönsted and Pedersen: <i>Z. physik. Chem.</i> , <b>108</b> , 185 (1924). Brönsted and Duns: <i>Ibid.</i> , <b>117</b> , 299 (1925). Brönsted and Volgvartz: <i>Ibid.</i> , <b>155A</b> , 2N (1931). Brönsted and Vance: <i>Ibid.</i> , <b>163</b> , 240 (1933). Pedersen: <i>J. Phys. Chem.</i> , <b>38</b> , 581 (1934). Bjerrum and Unmack: <i>Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.</i> , <b>9</b> , No. 1 (1929). Larsson: <i>Z. anorg. allgem. Chem.</i> , <b>155</b> , 247 (1926).
Decomposition of diacetone alcohol to acetone: $\text{H}_3\text{C}-\text{CO}-\text{CH}_2\text{O}-\text{CH}(\text{CH}_3)_2 \rightarrow 2(\text{CH}_3)_2\text{CO}$	Bases.	Akerlöf: <i>J. Am. Chem. Soc.</i> , <b>48</b> , 3046 (1926). Koelichen: <i>Z. physik. Chem.</i> , <b>33</b> , 129 (1900). French: <i>J. Am. Chem. Soc.</i> , <b>51</b> , 3215-25 (1929).
Decomposition of diacetone alcohol in aqueous solution of $\text{NaOH}$ or $\text{KOH}$ .	Hydroxyl ion catalyst alkali halides (salt effect); sodium phenolate buffer solution shows a very slight catalysis.	French: <i>J. Am. Chem. Soc.</i> , <b>51</b> , 3215-25 (1929).

Table 15 (Continued).

Reaction	Catalyst	Observer
Splitting off nitrogen from nitrosotriacetone amine with formation of phoron.	Bases.	Francis and co-workers: <i>J. Chem. Soc.</i> , <b>101</b> , 2358 (1912); <b>103</b> , 1722 (1913); <b>107</b> , 1651 (1915).
Acetone-iodine reaction.	OH' ion.	Dawson and Carter: <i>J. Chem. Soc.</i> , <b>1926</b> , 2282.
Enolization of acetic acid ester and acetic acid.	Base.	Pedersen: <i>J. Phys. Chem.</i> , <b>37</b> , 751 (1933). Pedersen: <i>Dissertation</i> , Copenhagen, 1932.
Isomerization of nitro-camphor.	Bases.	Lowry: <i>Trans. Far. Soc.</i> , <b>75</b> , 213 (1899).
$\text{C}_8\text{H}_{14} \begin{cases} \text{CHNO}_2 \\ \text{CO} \end{cases} \rightarrow \text{C}_8\text{H}_{14} \begin{cases} \text{C=NOOH} \\ \text{CO} \end{cases}$		
Autoracemizations.	Base.	Winther: <i>Z. physik. Chem.</i> , <b>56</b> , 719 (1906). Herz: "Schles. Gesellschaft Vaterland Kultur, Naturw. Sektion." 1911.
Isomerization of nitro-methane. $\text{CH}_3\text{NO}_2 \rightarrow \text{CH}_2=\text{NOOH}$ .	Base.	Pedersen: <i>Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.</i> , <b>12</b> , No. 1 (1932).

Decomposition of formaldehyde to  $\text{H}_2$  and formic acid; reduction of Fehling's solution is not carried out equally well by all aldehydes; benzaldehyde, glyoxal and formic acid do not reduce the Fehling's solution even under heating, while compounds capable of forming endiol groups, such as ascorbinic acid, glycol aldehyde, oxyacetone, glycerin aldehyde, acetoin and benzoin reduce  $\text{Cu}(\text{OH})_2$  readily in the cold; slower reduction follows with sugars; compounds capable of forming enols do not reduce readily in the cold; thus, for the reduction of  $\text{Cu}(\text{OH})_2$  to Cu the presence or formation of unsaturated hydrocarbon groups, endiol- or enol-groups is necessary; in case the enol form of formaldehyde favors the reaction, the specific action of Ca addition is expressed, and therefore not only the concentration of hydroxyl ions, but also the kind of cations determines the velocity of the formaldehyde reaction; the difference in the action of both bases consists in the fact that in the presence of NaOH only negatively charged formaldehyde ions are present (a complete ionization of the Na salt takes place), while in the presence of  $\text{Ca}(\text{OH})_2$  also the enolic form of formaldehyde is present although in a very small concentration:  
 $\text{HOCH}_2\text{ONa} = \text{Na}^+ + \text{HO} \cdot \text{CH}_2\text{O}^-$ .

With  $\text{Ca}(\text{OH})_2$  the reduction follows much more energetically than in the presence of NaOH; this is explained by the fact that enolization of formaldehyde is facilitated through  $\text{Ca}(\text{OH})_2$ .

Kurin: *Zhur. Obshchei Khim.*, **7**, (69), 2954-2963 (1937).

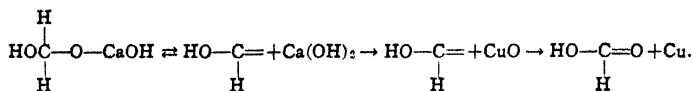


Table 15 (Continued).

Reaction	Catalyst	Observer
The induction period of the reaction corresponds to the very small concentration of the enolic form; however, only traces of metallic Cu formed catalyze strongly the dehydrogenation reaction of formaldehyde, whereby the Cu reduction is accelerated through nascent H; and after complete reduction of Cu, the development of H <sub>2</sub> takes place; the dismutation in concentrated formaldehyde solutions proceeds considerably faster in the presence of Cu(OH) <sub>2</sub> than of NaOH in dilute solutions; the difference is only small and the velocity in the presence of NaOH greater.		
Mutarotation of (1) glucose or (2) decomposition of nitramide; T. (1) 18°, (2) 15°.	Betain, salicylate, formate, benzoate, phenylacetate, acetate, propionate, trimethyl acetate, quinoline, pyridine, and [Co(NH <sub>3</sub> ) <sub>5</sub> OH] <sup>++</sup> .	Pfäuger: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 1513 (1938).

Table 16. Acids and Alkalies (both catalyzing agents for one reaction).

Reaction	Catalyst	Observer
Esterification and saponification.	Acids (and alkalies).	Scheele (1792).
Saponification of different esters.	Acids and bases.	Ostwald: <i>J. prakt. Chem.</i> , <b>28</b> , 449 (1883). Zengelis: <i>Ber.</i> , <b>34</b> , 198 (1901). Euler: <i>Z. physik. Chem.</i> , <b>36</b> , 640 (1901). Stieglitz: <i>J. Am. Chem. Soc.</i> , <b>30</b> , 29 (1908); <b>35</b> , 1774 (1913). Griffith and Lewis: <i>J. Chem. Soc.</i> , <b>109</b> , 67 (1916). Kendall and Booge: <i>J. Chem. Soc.</i> , <b>127</b> , 1768 (1925).
Saponification of $\gamma$ -lactone.	Acids and bases.	Henry: <i>Z. physik. Chem.</i> , <b>10</b> , 96 (1892). Taylor and Close: <i>J. Am. Chem. Soc.</i> , <b>39</b> , 422 (1917). Kailan and Neumann: <i>Z. physik. Chem.</i> , <b>101</b> , 63 (1922). Garrett and Lewis: <i>J. Am. Chem. Soc.</i> , <b>45</b> , 1091 (1923). Taylor and Close: <i>J. Phys. Chem.</i> , <b>29</b> , 1085 (1925).
Saponification of lactic acid lactide to lactyl lactic acid.	Acids and bases.	Kinger and Scrabal: <i>Monatsh.</i> , <b>43</b> , 507 (1922).
Conversion of starch into sugar.	Dilute acids (and alkalies).	Parmentier (1781). Kirchhoff (1811).
Hydrolysis of acid amides.	Acids and bases.	Reid: <i>J. Am. Chem. Soc.</i> , <b>21</b> , 284 (1894); <b>24</b> , 397 (1900). Acree and Nirdlinger: <i>J. Am. Chem. Soc.</i> , <b>38</b> , 489 (1907). Crocker: <i>J. Chem. Soc.</i> , <b>91</b> , 953 (1907). Sulo Kilpi: <i>Z. physik. Chem.</i> , <b>80</b> , 165 (1912). Euler and Rudberg: <i>Z. anorg. allgem. Chem.</i> , <b>127</b> , 244 (1923).
Hydration of carbonic acid anhydride.	Acids and bases.	Verkade: <i>Rec. trav. chim.</i> , <b>40</b> , 192, 199 (1920). Scrabal and Ringer: <i>Monatsh.</i> , <b>42</b> , 9 (1921). Scrabal: <i>Monatsh.</i> , <b>43</b> , 493 (1922).

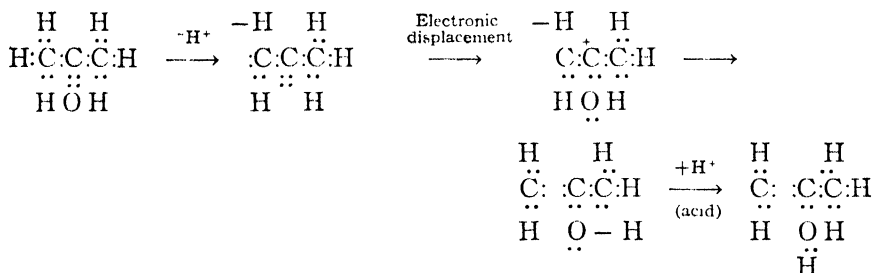
Table 16 (Continued).

Reaction	Catalyst	Observer
Catalytic isomerization.	Acids and bases.	Michael, Scharf and Voigt: <i>Chem. Zentr.</i> , 16, 1, 1015. Kekulé and Schröter: <i>Ber.</i> , 12, 2279 (1879). Gustavson: <i>Ber.</i> , 16, 958 (1883). Weiss and Downs: <i>J. Am. Chem. Soc.</i> , 44, 1118 (1922). Meerwein and Weber: <i>Ber.</i> , 58, 1266 (1925).
Enolization of acetone.	Acids and bases.	Dawson and co-workers: <i>J. Chem. Soc.</i> , 1926, 2282, 2872, 3166; 1927, 213, 458, 756; 1928, 543, 1239, 1248, 2844; 1929, 1217, 1884, 2530; 1930, 79, 2180; 1931, 2638; 1932, 2612; 1933, 49, 291.
Catalysis.	Acids and bases.	Brönsted: <i>Chem. Rev.</i> , 5, 231-38 (1928). Brönsted and Guggenheim: <i>J. Am. Chem. Soc.</i> , 49, 2554-84 (1927).
Mutarotation of various sugars.	Acids and bases.	Kuhn and Jakob: <i>Z. physik. Chem.</i> , 113, 389 (1924). Euler and Hedelius: <i>Biochem. Z.</i> , 170, 150 (1920). Euler and Laurin: <i>Svenska Vetensk. Akad. Ark. Kemi</i> , 7, 30 (1920). Brönsted and Guggenheim: <i>J. Am. Chem. Soc.</i> , 49, 2554 (1927). Lowry and Smith: <i>J. Chem. Soc.</i> , 1927, 2539.
Mutarotation of sugars.	Substances possessing either acidic or basic properties or both; oxygenated solvents, such as acetone and ethyl acetate, even in presence of water retard rather than accelerate mutarotation (even their "polar" character and relatively high dielectric constants do not enable them to develop any catalytic activity).	Lowry and Faulkner: <i>J. Chem. Soc.</i> , 127, 2885 (1925). Lowry: <i>Trans. Far. Soc.</i> , 24, 245-51 (1928).
Mutarotation of certain derivatives of tetramethyl glucose.	Alkalies and acids.	Baker: <i>J. Chem. Soc.</i> , 1928, 1979-87.
Mutarotation of glucose.	Three acids: HCl, chloroacetic and acetic; four bases: phenoxidian in Na phenolate, secondary phosphate ion in $\text{Na}_2\text{HPO}_4$ , acetate ion in Na acetate and chloroacetic ion in Na chloroacetate.	Smith, G. F. and Smith, M. C.: <i>J. Chem. Soc.</i> , 1937, 1413-20.
Acid-base catalysis in gas reactions, such as depolymerization of paraldehyde at 100° and 190°.	HCl and HBr, HI, HCOOH, $\text{CHCl}_2 \cdot \text{COOH}$ .	Bell and Burnett: <i>Trans. Far. Soc.</i> , 33, 355-363 (1937).
Depolymerization of dimer dioxycetone; T. 25°.	Acids: $\text{H}_3\text{O}^+$ , $\text{CH}_2(\text{CN})\text{COOH}$ , $\text{CH}_2\text{ClCOOH}$ , $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{OH})\text{COOH}$ and HCOOH; Bases: $\text{OH}^-$ , $(\text{CH}_3)_3\text{C} \cdot \text{COO}^-$ , $\text{CH}_3\text{COO}^-$ , $\text{C}_2\text{H}_5 \cdot \text{CH}_2\text{COO}^-$ , $\text{CH}_2=\text{CH} \cdot \text{COO}^-$ , $\text{HCOO}^-$ , $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{OH})\text{COO}^-$ , $\text{CH}_2\text{ClCOO}^-$	Bell and Baughan: <i>J. Chem. Soc.</i> , 1937, 1947-1953.

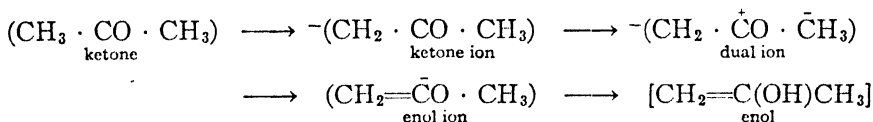
Table 16 (Continued).

Reaction	Catalyst	Observer
Catalysis between dimethyl-, diethyl-, di- <i>n</i> -propyl-, diisopropyl- and di- <i>n</i> -butylphosphite and iodine; T. 20–30°; the monomolecular velocity constants <i>K</i> are calculated; the activation energy of all esters is of the order of magnitude (15,000–17,000 cal.); the differences of <i>K</i> <sub>1</sub> are based on differences in the action constants <i>a</i> , methyl ester <i>K</i> = 4.10 <sup>-4</sup> , isopropyl ester <i>K</i> = 2.10 <sup>-6</sup> ; the process determining the velocity of the reaction is the prototropic conversion to which an acid, as well as a base catalysis is subjected; in the case of acid catalysis the velocities are 3:1 to 15:1; in base catalysis <i>K</i> <sub>6</sub> is greater by 3 tenths degree; the reaction velocity in the case of diisopropylphosphite is considerably smaller than that of di- <i>n</i> -butyl ester.	(H <sub>3</sub> O) <sup>+</sup> ions, acids as well as bases; cacodylic acid, H <sub>3</sub> PO <sub>4</sub> , citric acid, iodoacetic acid, glycolic acid, acetic acid, and propionic acid.	Nylén: <i>Z. anorg. allgem. Chem.</i> , <b>253</b> , 161–182 (1938).

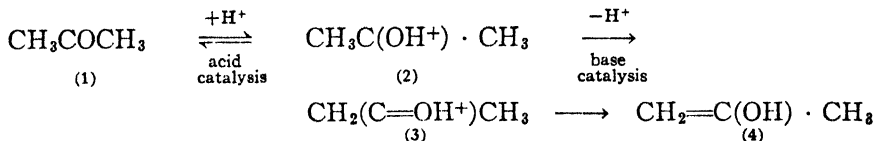
the keto-enol conversion of acetone according to the following scheme, when catalyzed by a *base*:



in this scheme:

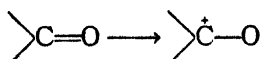


Pedersen<sup>164</sup> claimed the following scheme for acid catalysis of the keto-enol conversion of acetone:



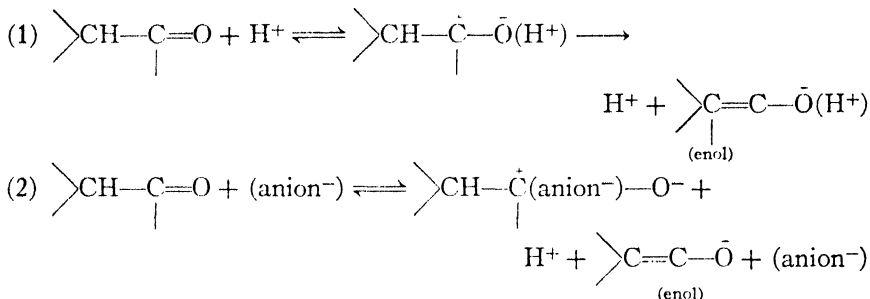
In this reaction sequence, Pedersen considers transition (2) to (3) the slowest step and the place where the catalytic rearrangement takes place.

Lowry postulates that the keto group is capable of reversing readily under electronic displacement of C atom to O atom from the homopolar into the semipolar binding state:





Taking into consideration Hinshelwood's conception of homogeneous gas catalyses in the decomposition of ether, according to which the catalyst (iodine molecule) transfers the activation energy to the future place of splitting of the reacting molecules, Watson and his co-workers<sup>218</sup> interpreted the keto-enol conversion as one incorporating the prototype of a tautomerization caused by the migration of the H<sup>+</sup> atom, the rearrangement taking place in the case of the H<sup>+</sup> ion (1) and the anion (2) catalyses, and illustrated it by means of the following scheme:

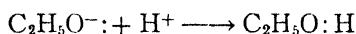


The discovery and the isolation of the hydrogen isotope has permitted the following changes to take place by a reattachment (place change) of protons. Reitz<sup>177</sup> measured the bromination of acetone catalyzed by H<sup>+</sup> ions in both light and heavy water and in H<sub>2</sub>O-D<sub>2</sub>O mixtures at 25° from the change in the destruction of the reaction solution by means of a selenium photocell. For these experiments, both light and heavy acetone was used, as well as equilibrium acetone, *i.e.*, acetone in which an exchange equilibrium with D<sub>2</sub>O containing water is established after heating the reaction solution for 10 hours up to 80°. It has been ascertained (1) that enolization proceeds 2.1 times faster in D<sub>2</sub>O in the presence of D<sub>3</sub>O<sup>+</sup> ions than in water in the presence of H<sub>3</sub>O<sup>+</sup>; this seems to indicate that the concentration of the complex, which has been formed by the addition of hydrogen ions to the oxygen of the ketone in equilibrium with acetone, is greater in the case of D<sub>2</sub>O than in H<sub>2</sub>O. (2) That the acceleration effect in D<sub>2</sub>O is found to be the same for light as well as for heavy acetone; however, the latter, under equal conditions, namely equal content of D<sub>2</sub>O in the solvent, always enolizes 7.7 times slower than the light acetone; in other words, the setting free of a deuteron from carbon proceeds with just as much difficulty as that of a proton. (3) That in a H<sub>2</sub>O-D<sub>2</sub>O mixture, the enolization velocity does not increase linearly with D<sub>2</sub>O content in water; the changes are rather slower for the lower D<sub>2</sub>O content than for the higher D<sub>2</sub>O content. (4) That the bromination velocity of acetone under equal conditions has been found to be equal to the exchange velocity for the first hydrogen atom.

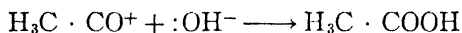
Bonhoeffer and Reitz,<sup>27</sup> discussing the mechanism of hydrogen ion catalysis, state that in general all reactions catalyzed by hydrogen ions contain compounds with O, N, or double bond C atoms and, therefore, have a tendency to add hydrogen ions with formation of oxonium, ammonium, and similar compounds. It has also been emphasized that very little is

known about the time necessary for establishing a proton addition equilibrium in the course of a hydrogen ion catalysis, and that perhaps in reactions which proceed faster in  $D_2O$  than in  $H_2O$  a previous equilibrium has been established, which is not the case in reactions slowed down by  $D_2O$ .

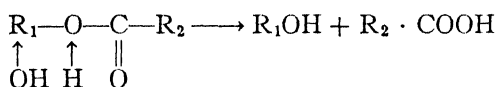
In connection with the theory of acid and base catalysis which is interpreted as a phenomenon followed by the addition to or the splitting off of protons, whereby an electronic displacement is induced causing a change in valence conditions within the substrate molecules, hydrolytic reactions have also been considered. Schwab, in his book,<sup>187</sup> discusses a typical catalysis of a hydrolysis, namely, ester saponification, and states that the valence electron pair of the ester  $H_3C \cdot CO : OC_2H_5$  is completely drawn over to the ethoxy half by the addition of an acid proton with formation of an alcohol:



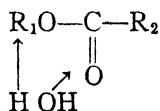
while the remaining acid residue combines with a hydroxyl ion through its valence electron pair to an acid molecule:



Kinetic measurements on esters of various composition made some investigators believe that splitting of a carbonic acid ester by its saponification occurs at the anhydride binding place, while that of a sulfonic acid ester takes place at the etheric binding place.<sup>122, 127, 138</sup> On the other hand, Skrabal's experiments<sup>190, 191</sup> made him believe that in general the splitting proceeds at both binding places, but to a different extent. Polanyi and Szabo<sup>166</sup> attempted to solve this problem by investigating amyl acetate subjected to a basic saponification in water rich in the oxygen isotope  $O^{18}$ . They postulated that if the splitting mechanism is etheric:



then the resulting alcohol should show an enrichment in the oxygen isotope in its hydroxyl group, corresponding to that of water in solution. In the case of the anhydric splitting:



the oxygen of the alcohol formed should contain the normal isotope (atomic weight close to 16). The experimental results indicated that the amyl alcohol obtained as a result of saponification contained the normal oxygen isotope ratio, and therefore the splitting of amyl acetate should take place at the anhydric binding place.

It has been emphasized by Skrabal<sup>190, 191</sup> that acid saponification of ethers is faster if the alcohol components contained in them are more basic.



In accordance with this, ethers of tertiary alcohols should saponify more readily by acids than ethers of secondary and primary alcohols because of the decided basic nature of the first.

On the other hand, ethers of alcohols of an acid character, such as ethers of phenols, namely, nitrophenols, are adapted for alkali saponification. In other words, the acid and base strength of the reacting components determines the saponification constants. According to this principle, acid anhydrides should be hydrolyzed considerably faster through bases than through acids. Because of the fact that in ester hydrolyses both alcohols and carboxylic acids are formed, they are accelerated through acids as well as bases. Esters stand between ethers and alcohols, and the velocity constants of their acid or base saponification depend on the acidic or basic nature of their acid as well as their alcohol component. The velocity of acid hydrolysis increases with increasing basicity of alcohols, and the velocity of basic hydrolysis increases with increase in the acid nature of the alcohols. Esters of a tertiary alcohol, such as tertiary butyl acetate, and an enol ester, such as vinyl acetate, serve as examples of the first case. Acetates of phenol and methylene glycol serve as examples of the second case; the alcohol  $\text{CH}_2=\text{CHOH}$ , as a result of dual ions formation, possesses pronounced acidic as well as basic properties.

Westheimer and Cohen<sup>219a</sup> studied the decomposition of diacetone alcohol in buffer solutions by various amines and found that molecular amounts of trimethylamine and triethylamine have no influence on the course of the reaction; therefore, the condensation of aldol is not an example of base catalysis. These experiments were conducted in order to clarify the contradiction which arose through the experiments of Miller and Kilpatrick<sup>184a</sup> and those of French.<sup>93a</sup> The first investigators observed in the decomposition of diacetone alcohol catalyzed by amines that with an increase in the concentration of the buffer solution an increase in the acceleration of the reaction also takes place, and deduced therefrom that the aldol condensation is an example of a general base catalysis. French, on the contrary, found that the decomposition reaction in a phenol-phenolation buffer solution depended solely on the OH ion concentration.

Osborn<sup>160</sup> and Skrabal<sup>192</sup> believe that acid and base catalysis may be explained by intermediate compound formation. They divided the reaction  $A \longrightarrow B$  into the following partial reactions:



where  $K$  is the proportion of the catalyst, and  $Z$ , the intermediate compound. They express the kinetics of the reaction in dilute aqueous solutions, for a series of simultaneous actions, as follows:

$$\frac{d[B]}{dt} = (K_w + K_a[H'] + K_b[OH'])[A] \quad (2)$$

where the bracketed symbols represent concentrations;  $K_a$ , the velocity

constant of the reaction promoted by  $H^+$  ions, or "acid reaction";  $K_b$ , the velocity constant of the reaction promoted by  $OH^-$  ions, or "base reaction," and  $K_w$ , the velocity constant of the uncatalyzed reaction, or "water reaction." Thus from equation (1) is deduced the velocity for the complete reaction:

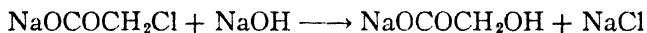
$$\frac{d[B]}{dt} = K [K][A] \quad (3)$$

With equation (1), Skrabal associates the idea that every transformation between the two components proceeds in the opposite direction and that, if so, the reacting substance  $A$  must have basic properties, if the catalyst  $K$  is an acid, and for the reacting substance having acid properties the catalyst is a base. He thus illustrates the thought that typical ethers having no acid properties, but only basic ones (oxonium bases), show a hydrolysis catalyzed by acids. Esters which are both bases and acids behave accordingly on hydrolysis, since the latter is accelerated both by acids and by bases. With respect to the nature of the intermediate compound  $Z$ , he states that it must be either a salt formed from an acid, or a base, or an ion. Difficulty arises, as salt formation or neutralization may proceed rather imperfectly, and also because the intermediate product may be present in small concentration and the initial reaction substance  $A$  can be only a weak base or a weak acid or an ampholyte. From the kinetic point of view, Skrabal differentiated two types of intermediate compounds: (1) the Arrhenius type, which is in chemical equilibrium with the initial materials, and (2) the van't Hoff type<sup>212</sup> not controlled by chemical equations (assumed for many reactions of a lower order) and rather similar to the "critical complex" claimed by Marcelin<sup>153</sup> and also by Brönsted.<sup>31</sup> The second type of intermediate compounds has greater instability than the first.

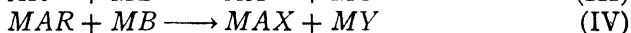
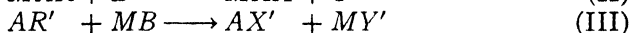
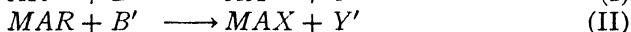
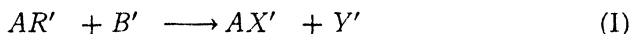
#### SALT EFFECT

The fact that addition of a neutral salt to a reaction system subjected to acid or base catalysis may change the conversion velocity considerably is known from the classical example found by Arrhenius,<sup>10</sup> namely, the velocity of inversion of cane sugar in a weak acid such as acetic is increased by about 30 per cent by the addition of 10*N* sodium chloride. If sodium acetate instead of sodium chloride is added, then a decrease in the velocity of inversion is effected, but to a much less extent than that corresponding to a simultaneous decrease in the  $H^+$  ion concentration calculated by the mass action law. In other words, in the case of sodium chloride there is an accelerating "salt effect." In the case of the sodium acetate, the effect does not follow exclusively from the increase in the electrolyte content as in the case of sodium chloride, but also from a catalytic side action of the acetate ion. According to the classic law of mass action, the introduction of foreign ions would not influence the catalyst concentration and produce a change in partial velocities of the catalytic *brutto* effect.

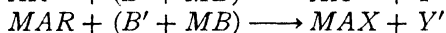
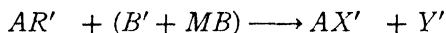
The significance of neutral salts as catalysts has been recognized by Seuter,<sup>188</sup> who assumed that salts like sodium chloride, sodium nitrate, or sodium sulfate increased the velocity of the reaction:



because they increase the reaction ability of the hydroxyl ions in some manner, while they are without action upon the reaction ability of the chloracetate. Holmberg,<sup>126</sup> in his study of cation catalysis, believed that the influence of a strong base upon a salt of a halide-substituted acid, an ester acid, lactic acid, etc., is based on the fact that the action of the undissociated salt on the hydroxyl ion is more rapid than that of the corresponding anion and that the reactivity of the undissociated base (strong) is equal to that of the hydroxyl ion. The latter conception was considered by Holmberg<sup>125</sup> to be confirmed by the fact that the reaction between chloracetate and potassium xanthogenate is accelerated catalytically by the cation, while this is not the case for the same reaction with chloracetamide. Thus the xanthogenate molecule and xanthogenate anion react with practically equal rates with one and the same acetic acid derivative, but the velocity is higher when this derivative is a chloracetate molecule than when it is a chloracetate ion. The general scheme for reactions to be considered in cation catalysis, according to Holmberg's viewpoint, is as follows:



Equations I and III and II and IV may be combined, thus:



The explanation of cation catalysis in a reaction between two strong electrolytes *MAR* and *MB* is based on the assumption that the substance *MAR*, in which the reacting radical is only a part of the corresponding anion, reacts in the undissociated form rather than in the form of its anion, while the electrolyte (*MB*), the anion of which is identical with the negatively charged reacting radical, reacts with almost equal speed, either as a molecule or as an anion.

Bredig<sup>30</sup> and Acree<sup>2</sup> considered that only the undissociated base molecules are catalysts in cation catalysis. Korczynski<sup>183</sup> observed a definite catalytic action of salts of certain metals in reactions of organic compounds, and so did Baudisch.<sup>16</sup> Although the viewpoint commonly held, but not justified, is that ionic reactions are more rapid than reactions between electrically neutral molecules and that ions are chief participants in chemical transformations, deviations from ionic reactions, or "salt catalysis," has been definitely established. Changes produced in acid and base catalysis by the addition of salts were thought to be due to the

salts themselves. Since Arrhenius and Ostwald, the equation postulated for the reaction of ions is:

$$dx/dt = K_{\text{trans}}\alpha(A - x)^2$$

while that for the undissociated portion of the molecule, acid, base, or salt is:

$$dx/dt = K'_{\text{trans}}(1 - \alpha)(A - x)^2$$

Shröder and Acree<sup>189</sup> assumed that the question, whether the ionic or the molecular form of a given acid, base or salt is the constituent carrying out the transformation directly into the end product, is to be decided upon by the relative magnitude of the various constants as expressed by the equation:

$$K_N \longrightarrow [K_i\alpha + K_m(1 - \alpha)][1 + (f)C_{\text{salt}}]$$

in which the second term of the equation is the factor of "salt catalysis," while the first term corresponds to the activity of ions and molecules in normal solutions having the ionization  $\alpha$  and the velocity  $K_N$ .

The classic dissociation theory predicts velocity changes only in cases in which the added salts contain a mutual ion and change directly the concentration of hydrogen or hydroxyl ions. Milner<sup>155</sup> and later Bjerum<sup>22</sup> introduced a special conception—that of "activity"—to the known thermodynamic anomalies of strong electrolytes (such as anomalous freezing and boiling point displacement, anomalous potentials in electric chains); the term was to be used instead of concentrations determined from the classic mass action law.

In order to find a reason for the action of a neutral salt upon the reaction velocity in the case of saponification of an ester, Akerlöf<sup>4</sup> combined velocity measurements at constant titer acidity with measurement of hydrogen ion activity. He derived the following formula for the relationship between velocity and activity:

$$K = C\alpha \cdot f(n)\sqrt[3]{\alpha}$$

where  $K$  is the reaction velocity;  $n$ , the titer acidity, and  $\alpha$ , the hydrogen ion activity. This formula has been found to hold true for all concentrations of the catalyst and is not influenced by the nature and concentration of the salt present. It has been claimed that this formula is valid not only for the saponification of esters, but also for the inversion of sugars and other closely related reactions; and Akerlöf assumed this to be proof that the theory of catalytic activity of undissociated molecules is not correct. Akerlöf asserted that salt molecules have no activity of their own, but that they are only the reason for changes in the activity of catalysts. He also answered the question regarding the manner in which neutral salts actually change the activity of the catalyst by stating that the water layers of the hydrogen ion are changed by the addition of neutral salts. Thus the concentration of hydrogen ions is kept constant, but their activity is changed. According to this viewpoint, the hydration numbers are not definite numbers, and it is the varying force with which

various ions attract the water molecules that causes the different neutral salt actions. From a comparison of hydration numbers made available by the investigations of Remy<sup>179</sup> and Washburn and co-workers,<sup>215, 216, 217</sup> it has been deduced that the neutral salt action is the greatest for ions which are hydrated to a greater extent. Against this hypothesis stands the equality of the neutral salt action for all nitrates, while in the case of chlorides, the action does change from one salt to the other.

Goldschmidt,<sup>104, 105</sup> Bredig,<sup>30</sup> Snethlage,<sup>194, 195</sup> Millar,<sup>154</sup> Braune<sup>29</sup> and Taylor<sup>206, 207</sup>, in their hypotheses of catalytic activity of undissociated molecules, postulate that the salt changes the activity of the catalyst, but has no activity itself; it appears that the activity of a neutral salt should change with the catalyst concentration. If  $K_m$  denotes the catalytic activity and  $n_m$  the concentration of the undissociated neutral salt, and  $K_H$  and  $n_H$  are the corresponding values for the catalyst, then the reaction velocity may be expressed:  $C = n_m K_m + n_H \cdot K_H$ . If  $n_H \cdot K_H$  is very small in a neutral salt solution, then the reaction velocity is also very small, and independent of the salt concentration, as was ascertained by Henderson and Kellogg.<sup>112</sup> Bjerrum's hydration theory,<sup>23</sup> together with Arrhenius' viewpoint<sup>8, 9</sup> that the neutral salt action is to be regarded as a result of the influence of salts upon the osmotic pressure of reacting bodies, provided another explanation for the mechanism of the salt action. Assuming, according to the hydration theory, that ions are surrounded by a layer of water molecules, it was thought that the added neutral salt withdraws a part of these water molecules from the ions of the catalyst, using them for its own ions. The osmotic pressure of the catalyst increases and, as the layer becomes smaller, the probability for the formation of an intermediate compound, without which a catalytic reaction does not take place, is also lessened.

Coinciding with the above explanation of the action of a salt were the findings by Spohr<sup>198, 199</sup> that the action of neutral salts decreases with an increase in temperature, because the hydration of ions decreases with increasing temperature and the requirement for water molecules effected by the introduction of salt ions becomes smaller. In the case of a hydrogen ion surrounded by a layer of eight molecules of water, the salt action upon the hydrogen ions should be much greater for a low concentration than for a high one because, in the latter case, the salt ions are influenced by a greater number of ions and therefore the change in the activity of a single ion is not great.

In an alkaline solution the activity of hydroxyl ions was found by Harned<sup>110</sup> to increase with addition of alkali chlorides, while a decrease in the reaction velocity of an alkaline solution by halide salts, according to Arrhenius,<sup>8, 9</sup> is not in agreement. A similar explanation of the action of neutral salts has been offered by Armstrong,<sup>6</sup> Caldwell,<sup>46</sup> and Whymper,<sup>220</sup> who considered the possibility of an increase in the concentration of the catalyst and simultaneously an increase in the reaction velocity being brought about through the formation of a hydrate by neutral salts which withdraw water from the reaction solution.

In many cases evidence has been produced that in acid and base

(Text continued in page 213)

Table 17. Acid-Salt Action and Base-Salt Action in Catalytic Reactions.

Reaction	Catalyst	Observer
Inversion of sugar.	Dilute $\text{CH}_3\text{COOH} + \text{NaCl}$ .	Arrhenius: <i>Z. physik. Chem.</i> , 226 (1889); 5, 1 (1890).
Inversion of cane sugar (a positive primary salt effect).	Catalyzed by 0.1 <i>N</i> $\text{HCl}$ at 30° in the presence of $\text{NaCl}$ , $\text{BaCl}_2$ , $\text{K}_2\text{SO}_4$ , or $\text{MgSO}_4$ solutions.	Floyd: <i>J. Phys. Chem.</i> , 35, 2968-84 (1931); refer also to Brønsted and King: (Refer to C. 1926 I. 577).
Catalytic decomposition of $\text{H}_2\text{O}_2$ .	$\text{K}_2\text{Cr}_2\text{O}_7 \cdot (\text{NH}_4)_2\text{CrO}_5$ decomposes in alkaline or neutral solution, giving off oxygen without reduction of chromium to trivalent state; chromium chromate.	Riesefeld: <i>Ber.</i> , 38, 1888 (1905). Spitalsky: <i>Z. anorg. allgem. Chem.</i> , 53, 184 (1907). Robertson: <i>J. Am. Chem. Soc.</i> , 48, 2072 (1926). Berthelot: <i>Compt. rend.</i> , 108, 24 (1889). Schönbein: <i>J. prakt. Chem.</i> , 80, 257 (1860).
Catalytic decomposition of $\text{H}_2\text{O}_2$ .	Neutral salt action of Fe ions.	Kiss and Lederer: <i>Z. physik. Chem.</i> , 129, 186-198 (1927).
Decomposition of nitramides, $\text{H}_2\text{NNO}_2$ .	$\text{H}_2\text{O}$ promotes the reaction slowly, but basic molecules, such as aniline, hydroxyl ions of cobalt amines, e.g., $[\text{Co}(\text{NH}_3)_5\text{OH}]^{2+}$ accelerate strongly.	Brønsted and Pedersen: <i>Z. physik. Chem.</i> , 108, 185 (1924).
Catalytic dissociation of $\text{H}_2\text{O}$ .	Acid and salt action.	Dawson: <i>J. Chem. Soc.</i> , 1927, 1290-97.
Catalytic decomposition of nitrosotriacetamine.	$\text{NaOH} + \text{alkali buffer}$ (secondary kinetic salt effect; change of $\text{OH}^-$ ).	Kilpatrick, Jr.: <i>J. Am. Chem. Soc.</i> , 48, 2091-99 (1926).
Catalytic decompositions.	Neutral salts.	French: <i>J. Phys. Chem.</i> , 32, 401-14 (1928).
Oxidation of cotton seed oil.	Base-forming metals and their salts: $\text{CaSO}_4 < \text{CaCO}_3 < \text{CaO} < \text{PbSO}_4 < \text{PbCO}_3 < \text{PbO}$ (rapid oxidation obtained for $\text{PbO}$ ).	Slansky: <i>Chem. Umschau Fette, Öle, Wachse, Harze</i> , 31, 449-50 (1924).
Oxidation of $\text{HBr}$ .	Chromic acid + salts.	Bobtelsky and Rosenberg: <i>Z. anorg. allgem. Chem.</i> , 177, 137-44 (1928). Bobtelsky and Kaplan: <i>Ibid.</i> , 177, 119-33 (1928).
Reduction of $\text{HClO}$ .	$\text{HBr} + \text{Ru}$ salts.	<i>J. Am. Chem. Soc.</i> , 51, 786-94 (1929).
$\text{NaOCCOCH}_2\text{Cl} + \text{NaOH} \rightarrow \text{NaOCCOCH}_2\text{OH} + \text{NaCl}$	$\text{NaCl}$ , $\text{NaNO}_3$ , or $\text{Na}_2\text{SO}_4$ increased the reaction ability of the $\text{OH}$ ions.	Seuter: <i>J. Chem. Soc.</i> , 91, 460 (1907). Bredig: <i>Z. Elektr.</i> , 18, 539 (1912). Acree: <i>J. Am. Chem. Soc.</i> , 48, 361 (1912).
Mutarotation of glucose.	Salt effect.	Kuhn and Jakob: <i>Z. physik. Chem.</i> , 113, 389 (1924).
Catalysis.	Neutral salts.	Harned: <i>J. Am. Chem. Soc.</i> , 40, 1461-1481 (1918). Baudisch: <i>Biochem. Z.</i> , 106, 134-38 (1920).
Catalysis of organic compounds.	Neutral salts.	Korczynski: <i>Bull. soc. Chim.</i> , 29, 283-90 (1920).
Catalysis.	Hydroxyl ion and secondary kinetic salt effect.	Brønsted and King: <i>J. Am. Chem. Soc.</i> , 47, 2523-31 (1925).
Catalysis.	Fe salts.	Baudisch and Welo: <i>J. Biol. Chem.</i> , 61, 261-274 (1925).
Catalysis.	Secondary salt effect.	Dawson and Key: <i>J. Chem. Soc.</i> , 1928, 1239, 1248. Brønsted and Pedersen: <i>Z. physik. Chem.</i> , 108, 185 (1924). Brønsted and Teeter: <i>J. Phys. Chem.</i> , 28, 579 (1924). Brønsted and King: <i>J. Am. Chem. Soc.</i> , 47, 2523 (1925). Dawson: <i>Trans. Far. Soc.</i> , 24, 640 (1928).

Table 17 (Continued).

Reaction	Catalyst	Observer
Self-esterification of trichloroacetic acid.	10% accelerated by its own sodium salt.	Goldschmidt: <i>Z. Elektr.</i> , <b>15</b> , 4 (1909).
Catalysis of ethyl or methyl diazoacetic ester.	$\text{CH}_3\text{COOH}$ , trinitrobenzoic acid, sulfosalicylic acid, trichlorobutyric acid and picric acid + salts.	Braune: <i>Z. physik. Chem.</i> , <b>85</b> , 170 (1913). Bredig: <i>Z. Elektr.</i> , <b>18</b> , 535 (1912).
Saponification of ester.	Neutral salt action (the conc. of H ions is kept constant, but their activity is changed).	Akerlöf: <i>Z. physik. Chem.</i> , <b>98</b> , 260 (1921).
Ketone splitting of acetic acid ethyl ester.	Normal alkali sulfates act upon alkali bisulfates.	Goodhue and Dunlap: <i>J. Am. Chem. Soc.</i> , <b>50</b> , 1916-22 (1928).
Catalysis of acetic acid acetate mixtures.	Acid and salt action.	Dawson and Key: <i>J. Chem. Soc.</i> , <b>1928</b> , 1248-57.
Esterification of acids, such as acetic, propionic, etc. with various alcohols, such as ethyl, isopropyl and <i>n</i> -propyl.	$\text{H}_2\text{SO}_4$ , $\text{H}_3\text{PO}_4$ , $\text{NaHSO}_4$ , $\text{KHSO}_4$ , or $\text{Al}_2(\text{SO}_4)_3$ ; the catalytic action of bisulfates is assumed to be based not on their decomposition: $(\text{NaHSO}_4)_2 = \text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$ , but on the fact that they possess, similar to $\text{Al}_2(\text{SO}_4)_3$ , their own activity namely the one of the complex $\text{H}_2\text{SO}_4 \cdot \text{MeSO}_4$ in which the catalytic energy of the acid function is modified more or less by the inactivity of the neutral salt.	Senderens: <i>Compt. rend.</i> , <b>194</b> , 809-811 (1932).
Reaction between monochloroacetic acid and $\text{Na}_2\text{S}_2\text{O}_3$ : $\text{CH}_2\text{ClCOO}^- + \text{S}_2\text{O}_3^{2-} \rightarrow \text{CH}_2\text{S}_2\text{O}_3\text{COO}^- + \text{Cl}^-$ ( $\text{Na}_2\text{S}_2\text{O}_3 = 0.0105$ molar solution) ( $\text{CH}_2\text{ClCOONa} = 0.015$ molar solution) total ion conc. = $\mu 0.136$ respectively, 0.547; the specific anion action disappears for low ion concentrations ( $\mu = 0.136$ ).	KCl, NaCl, LiCl, $\text{BaCl}_2$ , $\text{SrCl}_2$ , $\text{CaCl}_2$ , $\text{LaCl}_3$ , $\text{NaNO}_3$ and $\text{Na}_2\text{SO}_4$ ; the reaction velocity increases with increasing mobility in the series: $\text{K}' > \text{Na}' > \text{Li}' > \text{Ba}'' > \text{Sr}'' > \text{Ca}'' > \text{Br}' > \text{Cl}' > \text{NO}_3' > \text{SO}_4''$ ; with respect to charge; action of $\text{Ca}''$ is 1.5 times greater than that of $\text{La}'''$ and about 3.25 times greater than that of $\text{Na}'$ .	Bekier and Zelazwa: <i>Roczniki Chem.</i> , <b>14</b> , 994-1003 (1934).
Catalytic reaction between Na monochloroacetate and $\text{Na}_2\text{S}_2\text{O}_3$ at $50^\circ$ .	KCl, NaCl, LiCl, $\text{BaCl}_2$ , $\text{SnCl}_2$ , $\text{MgCl}_2$ , $\text{NaBr}$ , $\text{NaNO}_3$ and $\text{CH}_3\text{COONa}$ (conc. 0.035-0.55); the salt acceleration effect increases with the ion mobility in the series: $\text{K}' > \text{Na}' > \text{Li}''' > \text{Ba}'' > \text{Sr}'' > \text{Ca}'' > \text{Mg}''$ ; $\text{Br}' > \text{Cl}' > \text{NO}_3 > \text{CH}_3\text{COOH}'$ .	Bekier: <i>Roczniki Chem.</i> , <b>16</b> , 64-68 (1936).
Hydrolysis of bromoacetic acid ions in alkaline solution. $\text{Br} \cdot \text{CH}_2\text{COO}' + \text{H}_2\text{O} \rightarrow \text{HO} \cdot \text{CH}_2\text{COO}' + \text{H}' + \text{Br}'$ $\text{Br} \cdot \text{CH}_2\text{COO}' + \text{H}_3\text{C} \cdot \text{COO}' \rightleftharpoons \text{H}_3\text{C} \cdot \text{CO}-\text{CH}_2 \cdot \text{COO}' + \text{Br}'$ $\text{H}_3\text{C} \cdot \text{CO}-\text{CH}_2 \cdot \text{COO}' + \text{OH}' \rightarrow \text{H}_3\text{C} \cdot \text{COO}' + \text{HO} \cdot \text{CH}_2\text{COO}'$	Sodium formate, acetate and tartrate (accelerate about 100%).	Seuter and Bulle: <i>J. Chem. Soc.</i> , <b>101</b> , 2528 (1912). Seuter and Ward: <i>Ibid.</i> , <b>101</b> , 2534 (1912).
Hydrolysis of ethyl acetate.	Acid and salt action.	Dawson and Lawson: <i>Ibid.</i> , <b>1927</b> , 2444.
Autocatalyzed ester hydrolysis.	Acid and salt action.	Dawson and Lawson: <i>Ibid.</i> , <b>1928</b> , 3218-27.
Hydrolysis of ethyl acetate.	Weak acids + NaCl.	Dawson and Lawson: <i>Ibid.</i> , <b>1929</b> , 1217.
Hydrolysis of ethyl acetate.	Monochloroacetic acid (acid-salt catalytic action).	Dawson and Lawson: <i>Ibid.</i> , <b>1929</b> , 393-401, 1884-95.

Table 17 (Continued).

Reaction	Catalyst	Observer
Ammonolysis of desmotropo-santonin(1) and tartaric acid diethyl ether(2) in liquid ammonia.	Acid catalysis in the presence of salts: $\text{NH}_4\text{Cl}$ , $\text{NH}_4\text{Br}$ and $\text{NH}_4\text{I}$ ; for (1) the corresponding velocities were 0.024, 0.015, 0.010; for (2) the catalytic activity drops in the sequence: $\text{NH}_4\text{Cl}$ , $\text{NH}_4\text{Br}$ , $\text{NH}_4\text{NO}_3$ , $\text{NH}_4\text{I}$ and $\text{NH}_4\text{ClO}_4$ .	Schattenstein: <i>Acta Physico-chim. U.R.S.S.</i> , <b>5</b> , 841-52 (1936).
Ammonolysis of various esters (santonin, desmotropo-santonin ethyl tartrate) in liquid ammonia.	Primary and secondary salt effects observed by adding ammonium salts in concentrated solutions; action of amides smaller than that of ammonium salts arranged in a series of increasing activity: acetamide, benzamide, formamide; for the anions, arranged according to increasing catalytic activity of their ammonium salts, the following series was obtained: $\text{ClO}_4^-$ , $\text{I}^-$ , $\text{NO}_3^-$ , $\text{Br}^-$ , $\text{Cl}^-$ ; the same series only in a reversed sequence was found for the osmotic coefficients and electric conductivity coefficients for ammonium salt solutions in liquid ammonia.	Schattenstein: <i>J. Am. Chem. Soc.</i> , <b>59</b> , 432-35 (1937); refer also to Schattenstein and Usskova: (Refer to C. 1936 I 293). Schattenstein, Gurjanowa and Plesskow: (Refer to C. 1937 II 2800).
Bromination of aliphatic acids. $(\text{CH}_3\text{CO})_2\text{O} + \text{Br}_2 \rightarrow \text{CH}_2\text{Br} + \text{COOH} + \text{CH}_3\text{COBr}$ scheme for the catalytic reaction: $\text{RCH}_2\text{COBr} + \text{Br}_2 \rightarrow \text{RCHBr} \cdot \text{COBr} + \text{HBr}$ $\text{RCHBr} \cdot \text{COBr} + \text{R} \cdot \text{CH}_2\text{COOH} \rightarrow \text{R} \cdot \text{CH}_2 \cdot \text{COBr} + \text{R} \cdot \text{CHBr} \cdot \text{COOH}$	Acetyl bromide (strong catalyst).  Action of red phosphorus is also attributed to the formation of small amts. of acid bromide according to the scheme: $\text{R} \cdot \text{COOH} + \text{HX} \rightarrow \text{RCOH} + \text{H}_2\text{O}$	Watson: <i>J. Chem. Soc.</i> , <b>127</b> , 2067-82 (1925).
Enolization of acetone.	$\text{CH}_3\text{COOH} + \text{NaCl}$ or $\text{NaNO}_3$ .	Dawson and Key: <i>J. Chem. Soc.</i> , <b>1928</b> , 1239. Dawson: <i>Trans. Far. Soc.</i> , <b>24</b> , 642 (1928).
Acetone iodination at 25°.	$\text{KH}_2\text{O}_4$ (0.04 mol solution in the presence of an inert salt, such as 0.04-3.54 <i>N</i> $\text{KCl}$ ; maximum ionization constant $19.1 \cdot 10^{-4} = 1$ g. mol/liter.	Dawson and Smith: <i>J. Chem. Soc.</i> , <b>1929</b> , 2530-39.
Acetone iodination at 25°.	$\text{HC}_2\text{O}_4$ ( $\text{KCl}$ added); in a conc. solution, the undissociated acid acts catalytically, while in a dilute solution dominates the catalytic action of hydrogen.	Dawson and Smith: <i>Ibid.</i> , <b>1930</b> , 79-85.
Iodination of phoron in a 50% alcoholic solution (the reaction proceeds through a keto-enol transformation).	$\text{HCl}$ , $\text{CH}_3\text{COOH}$ and buffer acetate; the catalytic action of the acetic acid molecule and the acetate ion has the smallest value.	Dawson and Spivey: <i>Ibid.</i> , <b>1931</b> , 2658-65.
Iodination of mesitylene oxide in 5% alcoholic solution.	The catalytic action of the acetic acid molecule and the acetate ion has values lying between those for phoron and acetone.	
Iodination of acetone.	The relative catalytic action of the acetic acid molecule and the acetate ion has the greatest value.	



Table 17 (Continued).

Reaction	Catalyst	Observer
Acetone-Iodine reaction.	Tartaric acid conc. ranges from 0.005-0.5 mol. liter; that of NaH tartrate, from 0.01-0.4; 0.05 M · C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> + xMNaHC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> (x = 0-0.4); 0.1 M · C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> + xMNaHC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> (x = 0-0.4); 0.1 MNaHC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> + xMNa <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> (x = 0-0.4); (velocity increases linearly with increase in conc. of catalyst).	Dawson and Spivey: <i>Ibid.</i> , <b>20</b> , 2612 (1932).
Reaction between persulfate and iodine.	S <sub>2</sub> O <sub>8</sub> '' + I'.	Price: <i>Z. physik. Chem.</i> , <b>27</b> , 474 (1898). Kiss and Bruckner: <i>Ibid.</i> , <b>128</b> , 71 (1927).
Homogeneous catalysis between persulfate and iodine ions:	Cu and Fe ions; Co-Cr-Mn-Ni ions represent a neutral salt action.	Kiss and Zonbary: <i>Rec. trav. chim.</i> , <b>46</b> , 225-39 (1927).
	$S_2O_8^{''} + 2I' \rightarrow 2SO_4^{''} + I_2$ $(1) S_2O_8^{''} + I' \rightarrow S_2O_8I^{'''} \\ (2) S_2O_8I^{'''} + I' \rightarrow 2SO_4^{''} + I_2$	
Catalysis of persulfate-iodine ion reactions.	Co complexes (the measurements of reaction velocities proved that the reaction follows Bronsted's neutral salt law).	Kiss, Bossanyi and Urmanczy: <i>Acta Lit. Sci. Regiae Univ. Hung. Francisco-Josephinae Sect. Chem. Mineral. Phys.</i> , <b>2</b> , 210-29 (1932).
Oxidation of iodides by persulfates:	KNO <sub>3</sub> , NaNO <sub>3</sub> , NH <sub>4</sub> NO <sub>3</sub> , Ba(NO <sub>3</sub> ) <sub>2</sub> , Al(NO <sub>3</sub> ) <sub>3</sub> , ZnSO <sub>4</sub> , MnSO <sub>4</sub> , (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ; the polyvalent salts, as well as the ions participating in the reactions, exert a strong accelerating effect (the effect of glucose is small); in the case of neutral salts, a "secondary salt effect" occurs; the catalytic influence of Fe and Cu is based on the acceleration of the ionic reaction.	Afanasiev: <i>Acta Physicochim. U.R.S.S.</i> , <b>6</b> , 893-904 (1937).
	$(1) K_2S_2O_8 + KI \rightarrow K_2SO_4 + KSO_4 + I$ $KSO_4 + KI \rightarrow K_2SO_4 + I; \\ 2I \rightarrow I_2; 2KSO_4 \rightarrow K_2S_2O_8$ $(2) K_2S_2O_8 + 2KI \rightarrow 2K_2SO_4 + I_2$	
In an acid medium the reaction proceeds more slowly than in a neutral medium.		
Oxidation of iodide by persulfate (homogeneous catalysis of the reaction between KI and K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ); it is assumed that the amino groups must be able to bind the molecule of the catalyst to the reacting substances; the basicity of the amine plays a certain part.	Various organic amines: the diamines NH <sub>2</sub> · NH <sub>2</sub> , NH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> and NH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub> have a slight influence on the reaction velocity; cystine has no influence; the presence of groups capable of reversible oxidation-reduction increases considerably the activity of the catalyst, for example, (1) <i>p</i> -phenylenediamine and (2) N, N-dimethyl- <i>p</i> -phenylenediamine; the first has a greater catalytic activity than the second; with respect to aniline hydrochloride, dimethylaniline, diphenylamine, tetramethyldiaminodiphenylmethane, tolidin, benzidin, amino azo benzene and <i>p</i> -amino phenol, a small effect on the reaction velocity has been found, and this led to the conclusion that catalytic activity decreases if only one amino group is present or if the distance between two amino groups becomes greater than the diameter of a benzene ring even when the compound contains a reversible oxydo-reductive system.	Afanasiev: <i>Acta Physicochim. U.R.S.S.</i> , <b>6</b> , 905-914 (1937).

catalysis the catalytic action was not due solely to H or OH ions or water and undissociated molecules. The increase in the catalytic power of strong acids on the addition of corresponding salts indicated the necessity of assuming the existence of specific salt effects. The fact that the great majority of catalytic reactions occur in solutions of various ions and materially alter their properties led to the recognition of the kinetic salt effect. Thus attempts were made to interpret the neutral salt effect in acid and base catalysis by considering changes in the dielectric constant, viscosity or other properties of the solvent, as well as the activity coefficients of the solutes dissolved in it.

The activity of a dissolved electrolyte depends not only on the number of its own ions per unit volume but also on the charge, valence, and concentration of ions otherwise present in the liquid space. With an increase in the concentration of the component carrying a charge, a marked change in mutual electrostatic action between ions within the liquid is brought about. The attraction or repulsion of ions influences greatly the space distribution and the free energy, and therefore the thermodynamic behavior, of a dissolved electrolyte.

The Debye-Hückel theory<sup>65, 66, 67, 126, 186</sup> evaluates theoretically the relationship between the values of activity coefficients and concentrations in the case of electrolytes and permits the calculation of activities as functions of density, charge sign and valency of components present in the reaction liquid. The nature of the solvent enters the corresponding formula expressing the relationship in the form of the dielectric constant and that of the single ion in the form of its electrostatic action interval. Thus a possibility is provided for calculating for a given acid or base catalysis all the velocity changes effected through variations in the ionic medium and the addition of foreign salts, or likewise through strong concentration changes of acid-catalyst or base-catalyst.

In studying the quantitative relationship between dissociation constants of weak acids and bases and their catalytic effect upon the glucose reaction, Brönsted described the kinetic salt effect as one superimposed on the main catalytic effect in acid and base catalysis. The salt effect Brönsted considered to be due to the change in the medium in which the reaction takes place, bearing a linear relationship to the concentration. If the reaction components *A* and *B* in the corresponding ionic medium possess the activity coefficients  $f_A$  and  $f_B$ , as well as concentrations  $C_A$  and  $C_B$  then, according to Brönsted,<sup>33</sup> the reaction velocity is not as in the classic theory  $K = C_A \cdot C_B$ , but  $C = C_A \cdot C_B \frac{f_A \cdot f_B}{f_{AB}}$ .

The hypothesis advanced by Brönsted emphasizing the existence of a quasi-complex or a combination between reactants and catalyst that is very unstable, and the fact that the rate of change of this complex is so slow that the mass equilibrium is always established, led to a simple formulation of the reaction velocity of a bimolecular reaction between molecules *A* and *B*:

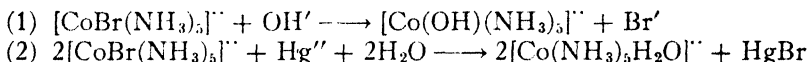
$$V = K \cdot C_A \cdot C_B \cdot \frac{f_A \cdot f_B}{f_{AB}}$$

in which the fraction  $\frac{f_A \cdot f_B}{f_{AB}}$  represents the probability factor for the formation of an intermediate complex  $AB$  by collision of molecules  $A$  and  $B$  and is termed "kinetic activity factor." In the case of acid-salt conversion catalysis of a substrate  $M$ , it is as follows:

$$K = C_M \cdot C_H + \frac{f_M \cdot f_{H^+}}{f_{MH^+}}$$

The kinetic activity factor is particularly sensitive towards changes in salt concentration and is found to vary in proportion to the square root of the salt concentration.

Brönsted's theory that the reaction velocity depends on the concentration of a critical complex in equilibrium with the reactants is put to a test when the primary reaction is between ions. Since the reactants and the critical complex have different electric charges, their activity coefficients will be affected to a different extent by changes in the ionic strength brought about by the addition of salts. Hence, since the concentration of the critical complex and the reaction velocity varied with the ionic strength, it appeared possible for Brönsted and Livingston<sup>39</sup> to study the following reactions for very dilute solutions, applying the theory of Debye and Hückel. The two bimolecular reactions chosen were:



The velocity of such reactions was expressed by an equation of the following type:

$$V = R_1\text{H}^+ + R_2\text{A}^- + R_3\text{OH}^- + R_4\text{HA} + R_5\text{H}_2\text{O}$$

in which  $R_1 - R_5$  denote specific activities of the various catalytic reactions. However, in order that such an equation should be justified, the actual concentrations of the reactants must be evaluated with accuracy, which is not an easy task in case of electrolytes. The question whether activities may be used in reaction velocity equations in place of concentrations cannot be answered with definite assurance.

Brönsted, studying the catalytic activity of partially ionized acids in salt solutions, definitely established the fact that there are two distinct effects involved in the catalytic behavior of inert salts. The first, called the "primary salt effect," is expressed in an increase in the catalytic activity of the hydrogen ion. The second, known as "secondary salt effect," is manifested by a change in the ionization constant of the acid. While the increase in the catalytic activity of the hydrogen ion proceeds continuously with the salt concentration, the ionization constant increases to a maximum value and then decreases. Thus, as a result of electrolyte addition, not only may the activity and the reaction ability be changed, but, by influencing the dissociation degree, the true concentration of  $\text{H}^+$  and  $\text{OH}^-$  ions may be displaced also. The primary salt effect has been recognized to be a direct kinetic effect. The secondary kinetic salt effect

was found<sup>38, 40, 41</sup> to depend not only upon the electric type, strength and concentration of the acid, but also upon the ratio in which the buffer constituents are present. The secondary salt effect is always accompanied by the primary effect. Addition of a neutral salt of the same anion alters the ionic strength of the medium and thus alters the reaction velocity at a given concentration. The linear salt effect is more pronounced in a concentrated solution (90 per cent in 3*N* NaCl) and the change in the catalytic efficiency may be studied independently only when the salt does not cause an alteration in the dissociation of the catalyzing acid. Thus the investigation is limited to strong acids, completely dissociated in a dilute solution.

Dawson and Lawson<sup>63</sup> maintained the point of view that the salt effect can be legitimately neglected and attempted to calculate the effect of undissociated acids in ester hydrolysis on this basis. Later, however, Dawson and Carter<sup>69</sup> and then Dawson and Key<sup>62</sup> recognized the existence of both salt effects and expressed the total catalytic effect produced by an acid in admixture with a salt by the equation:

$$V = V_h + V_a + V_m = K_h(H') + K_a(A') + K_m(HA) \quad (1)$$

in which  $V$  is the observed specific reaction velocity;  $K_h$ ,  $K_a$  and  $K_m$ , the catalytic coefficients, and the values in parentheses correspond to the concentration of the active constituents.

For a series of mixtures of acid and salt represented by the general formula:  $cHA = xMA$ , where  $c$  is constant and  $x$  is variable, Dawson and Dean<sup>61</sup> have shown that the velocity is a minimum when the hydrogen ion concentration has the value:

$$(H')_i = \sqrt{K_a K_c / K_h - K_m} \quad (2)$$

where  $K$  is the ionization constant of the acid. Denoting the velocity due to the positive and negative ions by  $U$ , the minimum value of the ionic reaction velocity has been expressed by:

$$U_i = 2\sqrt{(K_h - K_m)K_a K_c} \quad (3)$$

Expressing the hydrogen ion concentration for any mixture in terms of  $[H']$ , such that  $[H']/[H']_i = n$  and the ionic reaction velocity in terms of  $U_i$  so that  $U/U_i = r$ , it has been deduced by Dawson<sup>66</sup> that

$$r = 1/r(n + 1/n) \quad (4)$$

where  $r$  is the reduced ionic velocity and  $n$  the reduced hydrogen ion concentration. The applicability of the equation has been considered to be independent of the nature of the acid-catalyzed reaction, of the medium in which the reaction takes place, of the temperature, and of the nature and concentration of the catalyzing acid. The determination of  $n$  presumes a knowledge of  $[H']$  and  $[H']_i$ , the values of which may be calculated if the ionization constant of the acid  $HA$  is known. Dawson<sup>67, 68</sup> further showed that a generalized catalytic formula of the above type may be obtained which does not involve the knowledge of  $K$ .

In accordance with equation (1), the ionic reaction velocity may be expressed by:

$$U = V - K_m c = (K_h - K_m)[H'] + K_a K_c/[H'] \quad (5)$$

Assuming the acid in question is weak and the salt concentration in the acid-salt mixture is not very small, Dawson expressed the relationship between the hydron concentration and the salt concentration of the solution as:  $[H'] = K_c/[\bar{A}] = K_c/x$ . Substituting for  $(H')$  in equation (6) there is obtained:

$$U = (K_h - K_m)K_c/x + K_a x \quad (6)$$

According to this equation the ionic reaction velocity passes through a minimum value when the salt concentration has the value  $x$  given by the following equation:

$$x_i = \sqrt{(K_h - K_m)K_c/K_a} \quad (7)$$

Substituting the value of  $x_i$  in equation (6), the minimum reaction velocity is found to be:

$$U_i = 2\sqrt{(K_h - K_m)K_a K_c} \quad (8)$$

Expressing the salt concentration  $x$  in terms of the value characteristic of the minimum velocity for the mixture such that  $x = p x_i$ , the equation:

$$U = \sqrt{(K_h - K_m)K_a K_c}(p + 1/p) \quad (9)$$

may be written, where  $r = U/U_i = 1/2(p + 1/p)$ ;  $r$ , the reduced ionic velocity, and  $p = x/x_i$ , the reduced salt concentration. Thus equation (9) represents a general relationship between the ionic velocity and the salt concentration and is of the same type as equation (4). When  $p$  is sufficiently large, the term  $1/p$  may be neglected and  $U = 1/2 \frac{U_i X}{X_i}$  and

$$V = U + K_m C = K_m C + b x \quad (10)$$

In this equation the reaction velocity proves to be a linear function of the salt concentration.

Dawson and Carter<sup>59</sup> and Dawson and Lawson<sup>60</sup> proved this in their investigations of the velocity of iodination of ketones and in the hydrolysis of esters under the catalytic influence of weak acids in admixture with the corresponding salts, as represented by  $CHA + xMA$ . For these experiments, the plot of  $V$  against  $x$  gave curves falling rapidly to a minimum and following a linear course thereafter. The slope of the linear portion of the curve afforded a measure of  $K_a$ , corresponding to the catalytic coefficient for the acid anion  $A$ . The constant  $b$  in equation (10) can thus be identified with  $K_a$  and

$$K_a = 1/2 \frac{U_i}{X_i} \quad \text{or} \quad U_i = 2K_a X_i \quad (11)$$

analogous to the equation:  $U_i = 2(K_h - K_m)[H']$ , previously derived.

From equation (11) it follows that:

$$X_i = 1/2 \frac{U_i}{K_a} = (V_i - K_m C)/2K_a \quad (12)$$

By combining  $U_i = 2(K_h - K_m) \cdot [H^+]$  and  $U_i = 2K_a X_i$  by elimination of  $U_i$ , equation (13) is obtained:

$$X_i = (K_h - K_m)[H^+]_i / K_a = \sqrt{\frac{(K_h - K_m)K_c}{K_a}} \quad (13)$$

Since  $K_c$  is independent of the reaction catalyzed, the ratio of  $X_i$  values for two different reactions is given by the ratio of the corresponding values of:  $\sqrt{(K_h - K_m)/K_a}$ . For weak acids,  $K_m$  may be neglected in comparison with  $K_h$  and therefore the  $X_i$  ratio is given by the ratio of values of  $\sqrt{K_h/K_a}$ , that is, for a given catalyzing acid the ratio of the amounts of salt required for the reduction of the reaction velocities of two different reactions to their respective minimum values depends on the square root of the ratio  $(K_h - K_m)/K_a$ , and is independent of the concentration of the acid.

Dawson and Spivey<sup>64</sup> attempted to determine the catalytic coefficients from iso-catalytic data. Under the assumption that a buffer mixture for which the reaction velocity is a minimum is characterized by an equality of the catalytic effects, due to the hydrogen ion and the acid anion, the respective mixture termed *MV* has been described as an iso-catalytic buffer mixture. The corresponding reaction velocity, hydrogen ion concentration and salt concentration have been termed iso-catalytic data. The iso-catalytic effects were determined for three series of acetate buffers, assuming that the effects are due to the hydrogen ion, the acetate ion and the undissociated acid. The experiments established the fact that (1) the catalytic activity is to be attributed to a small extent to molecules of water; (2) the effect of the hydroxyl ion, although small at the iso-catalytic points, cannot be neglected, and (3) the complex acetate ion of the type  $HAc_2$  has also a small part in the iso-catalytic effect. Therefore, the total catalytic effect should be given by the following equation:

$$V = V_h + V_a + V_m + V_w + V_{OH} + V_{HAc}$$

*i.e.*, the observed minimum velocities should be corrected for the effects represented by  $V_w + V_{OH} + V_{HAc}$ ; thus the catalytic coefficients and the ionization constant of the acid are not independent of the salt concentration. Measurements should be carried out under a constancy of the ionic environment secured by the addition of a sufficient quantity of a chemically and catalytically inert salt to the reaction mixture.

Harned and Samaras,<sup>111</sup> interpreting the medium changes in homogeneous catalysis, expressed the velocity of the reaction between substances *A* and *B* by means of the equation:

$$V = \bar{K} C_A C_B \cdots F \quad (1)$$

in which *F*, denoting the kinetic factor, is postulated to be a function of

the concentration  $C_A$ ,  $C_B$ , etc. of some or all of the components present, and  $\bar{K}$ , a value independent of the concentration, but a function of temperature and consequently of the collision number.

Considering the thermodynamic requirements involved in direct and reverse reactions, it has been postulated that the kinetic factor contains the product of the activity coefficients  $\gamma_A$ ,  $\gamma_B$ , etc. of  $A$  and  $B$  and therefore:

$$V = \bar{K}' \cdot C_A C_B \cdot \cdot \cdot \gamma_A \gamma_B \cdot \cdot \cdot F' \quad (2)$$

If  $F'$  is the same for both direct and reverse reactions at the time when the system approaches the equilibrium, then the above equation leads to a consistent thermodynamic result. When  $F'$  equals unity, equation (2) expresses the activity rate theory. Brönsted advanced the interpretation of the kinetic factor  $F$  by using the equation:

$$V = \bar{K}' C_A \cdot C_B \cdot \cdot \cdot \frac{\gamma_A \gamma_B}{\gamma_{AB}} \cdot \cdot \cdot F'' \quad (3)$$

where  $F''$  is a unity and  $\gamma_{AB}$  is the activity coefficient of a hypothetical intermediate complex. This equation has been found very successful in accounting for the positive and negative salt effects in dilute solutions. However, it cannot be used for even an approximate calculation of the actual magnitude of the primary salt effect. This is particularly true in the case of homogeneous catalysis dealing with reactions between ions and neutral molecules.

On the basis of their equation, Harned and Samaras<sup>11</sup> defined the primary kinetic effect as the influence of either salt addition or a solvent change upon the kinetic factor  $F$ , while they regarded the secondary kinetic effect as a change in the concentration  $C_A C_B$  taking place upon the addition of salts or solvents.

Christiansen,<sup>46</sup> in his statistical theory, postulated for the velocity of reactions between two ions at constant temperature the following equation:

$$V = \bar{K}' C_1 C_2 e^{-\psi_1 Z_2 / RT}$$

in which  $C_1 C_2$  denote the concentration of two ionic reacting components;  $\psi_1$ , the potential at a distance  $r$  from the first ion, and  $Z_2$  the valence of the second. Substituting for  $\psi$ , the value obtained for the potential of an ion from the limiting law of the theory of Debye and Hückel, Christiansen showed that the equation for the case in question is:

$$V = \bar{K} C_1 C_2 \frac{\gamma_1 \gamma_2}{\gamma_2}$$

This equation having a statistical basis is experimentally valid for reactions between ions in dilute solutions.

Harned and Samaras modified their original equation for the velocity of the reaction to express medium changes in homogeneous catalysis by postulating the following formula:  $\bar{K} = K_0 C e^{-W/RT}$  in which  $\bar{K}$  is the velocity constant in the new medium;  $K_0$ , the velocity constant in the original medium before any change is effected;  $C$ , the concentration of

the catalyst and  $e^{-W/RT}$ , the Boltzmann distribution factor. Thus the "kinetic factor"  $F$  for medium effects in homogeneous catalysis has been thought to be  $e^{-W/RT}$ ;  $W$  has been assumed to be represented as follows:

$$-W_e = \bar{\Delta}F = RT \ln \frac{\gamma}{\gamma_1} = \frac{e^2 Z_I^2 4\pi (A_I - A_{II}) \delta V_{II} \cdot U_{II}}{2\alpha_1 D D_1}$$

and thus is a term associated with the dielectric constant change effected by a neutral substance or a salt.

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## Chapter 4

# The Activity of the Catalyst

### INTRODUCTION

The existence of a great number of catalysts, individual in nature and occurring in various forms, indicates the variety and extent of catalytic processes now known, as well as those potentially possible. Also, one and the same reaction may be catalyzed (accelerated or directed) by various catalysts. It is not wholly the catalyzing ability nor the particular behavior of a substance which makes it suitable as a catalytic agent. The question of the individuality of a catalyst and the reason for its action may be traced in the course pursued before and after it has influenced the yield and the character of the reaction products. Often the choice of a catalyst is based on its high accelerating ability, while its other properties, like sensitiveness to changes in the conditions of the reaction, the ease of regeneration after losing its original activity, or its ability to be stabilized against those changes through the addition of suitable admixtures or by activation treatment, are often overlooked. Not of least importance is the method by which a catalyst is prepared. It is well to know that small changes in the pretreatment of a catalyst may constitute very significant changes in its catalytic properties.

The function of a substance as a catalyst is governed by a number of factors which determine its efficiency and/or its activity. What is meant by the "activity" of a catalyst? How is it accounted for and how can it be estimated? It is supposed that various independent factors govern the activity of a catalyst. In the presence of a suitable surface, the catalytic action has been thought to take place only if a chemical compound which produces intermediate compounds is present at the same time.<sup>21</sup> In the preparation of substances as catalysts through a reaction, it has been shown that an active intermediate compound is one which manifests a catalytic activity and that continuation of the reaction converts it into a stable final product. In the case  $AB \longrightarrow A \text{ active} + B - G$ , and  $A \text{ active} \longrightarrow A \text{ stable} + G_2$ , the time interval in which the formation of active intermediate products reaches a maximum is expressed by  $t_m = (\ln K_1 - \ln K_2) / (K_1 - K_2)$ , in which  $K_1$  is the velocity in the formation of an intermediate product and  $K_2$  the velocity in the formation of the final product.<sup>303</sup> The probability of predetermining catalytic activity would be enhanced if a relationship between changes in the interatomic internal energy, according to thermodynamics, and the action of the catalyst could be established, and if the action of the catalyst and the action of chemical exchange corresponded to the constants of the law of mass action as a function of volume and mass of ingredients.<sup>218</sup> It has been supposed that catalytic activity

is connected with the chemical nature of the catalyst in the sense of increasing the solubility of hydrogen and increasing the affinity for oxygen.<sup>218a</sup> Constable<sup>87</sup> considered the presence of immovable atomic groups having strong specific external fields as one of the reasons for catalytic activity.

A solid body is composed of molecules, ions, or single atoms held together through saturation of the forces of adhesion. In the interior, these forces are saturated in all directions, but on the surface there are atoms varying in degrees of unsaturation. The kind of bonds, the chemical character of the substance, and the position of the atoms within the surface determine the magnitude of the residual forces.<sup>228</sup> It is generally conceived that a catalyst is a material which possesses certain points capable of promoting a chemical reaction, and that these points constitute a relatively small fraction of the total surface.<sup>22, 376, 377</sup> The catalytic activity is resident in atoms which, by virtue of their position with respect to neighboring atoms, possess unsaturated valence forces capable of effecting a distortion among the reacting molecules. The residual forces are smallest in the case of molecules situated in the middle of crystal surfaces, great for atoms at the edges, greater for atoms placed in corners and greatest in the case of atoms at edges and in corners. It has been suggested by Smith<sup>340</sup> that the activity of finely divided metals used as catalysts is due not only to their specific surface, but also to the physical state of the catalyst. In other words, an amorphous surface should be more active than a crystalline surface. Smith supposes that bonds, secondary valences or forces which hold atoms or molecules in correct crystallographic position in a crystal are directed inward toward the center of the crystal, whereas in an amorphous substance these bonds or forces are directed, at least partially, outward and take part in the formation of unstable intermediate compounds by which catalytic reactions proceed. Smith<sup>340</sup> believes that surface catalysts, such as platinum, nickel, or cobalt, should be prepared by a method giving principally the amorphous form and that a lower temperature of preparation will render a greater activity. On the other hand, it has been stated by Bowden and O'Connor<sup>62</sup> that the transition from a solid into a liquid state results in a sudden decrease in the catalytic activity. These investigators assumed that the total catalytic activity of a metal surface depends: (1) on the amount of surface available; (2) on the configuration of metal atoms in the surface, and (3) on the chemical nature of the metals. While the configuration of metal atoms in the surface is essential only under certain conditions, the activation of metal surfaces by oxidation, reduction, or sponge formation is based on the size of the reachable surface.

Steacie and Elkin<sup>365</sup> compared the catalytic activity of liquid and solid zinc in the decomposition of methanol and assumed that if the activity of a catalyst is based essentially upon the unevenness of the surface (active places, crystal edges, etc.), then it should decrease greatly upon the melting of the catalyst. To prove this, Steacie and Elkin determined the temperature dependence of the decomposition velocity of methanol vapor upon zinc to be between 360° and 440°, using a definite

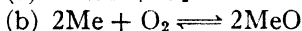
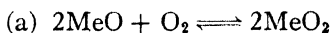
zinc surface, *i.e.*, 0.8 cm<sup>2</sup>, and as a measure of the catalytic activity, the time within which the total pressure increases by a certain percent. The results obtained showed that there was a continuous increase in the catalytic activity with an increase in temperature, but without a discontinuance at the melting point of zinc (420°). From this it was concluded that in general the catalytic activity of a solid substance cannot be ascribed to a limited part of its surface.

That the change in the structure of a catalyst may lead to a change in its catalytic properties is clear from the fact that the change in the parameters may be accompanied by a change in interatomic distances on the surface. The influence of this change may be expressed: (1) as purely geometrical, according to Balandin's "multiplet hypothesis"<sup>32, 33</sup>; or (2) it may be due to a rearrangement of surface forces as the result of a change in interatomic distances. When the structure of catalyzed molecules (molecules of organic compounds) is complex, then the relationship to the surface is determined, primarily, by the dependence of its geometrical structure and the structure of the surface of the catalyst. If the catalyst is considered in the light of Taylor's theory<sup>378</sup> as composed of active centers, that is, places of unsaturated valences which influence the reacting molecules in loosening their atomic bonds, then the catalyst binds to its surface those atoms which are set free, giving rise to surface compounds. In this way the resistance to reaction is diminished.<sup>273</sup> The second explanation concerning the influence of the structure of the catalyst upon its catalytic activity may be described as follows: With an increase in interatomic distance the free energy of surface atoms must increase, and with it the number of active centers which in turn would be reflected in an increase in catalytic activity. Attempts have been made to correlate the change in catalytic action with the change in atomic distances and surface forces.<sup>267</sup>

Lepin<sup>234a</sup> presents an interpretation of the passive state of metals, based on Faraday's theory of oxide films, and assumes that passivity of metals is caused by surface compounds, especially those of oxygen, whose properties are essentially different from products of the volume reaction. The smaller the lattice distance of atoms, the more difficultly are volume reactions brought about and the more favorable are the conditions for surface reactions. In discussing the catalytic activity of metals in the hydrogenation of benzene, Westling<sup>406</sup> arranged the metals in a series according to the shortest atomic distance in the lattice, for example, nickel, cobalt, copper, ruthenium, rhodium, iridium, osmium, palladium, and platinum, asserting that the activity decreases inasmuch as the shortest atomic distance moves away from both extremities.

In discussing the activity of catalysts from the standpoint of their affinity with respect to reacting components, *e.g.*, gases, Schenck<sup>313a</sup> points out the following five influential factors: (1) The degree of dispersion of the metal catalyst (powdered palladium and iron) (fineness of distribution increases their reactivity, while sintering reduces their effectiveness). Since fine dispersion strengthens the binding, it should not be recommended for catalytic processes (gases give compounds with the less

dispersed metals and may be poisons for the action of the catalyst). (2) Addition substances (substances with slight catalytic properties of their own may give excellent contact masses on the addition of suitable promoters). Schenck explains the catalytic action of mixtures of catalysts as well as promoters by considering the chemical nature of the addition, and links it with processes in a solid state. When a solid substance is used as an addition substance (independently of whether mixed crystals or compounds or adsorption products are formed), it reacts with the metal (Me) or metal oxides (MeO or MeO<sub>2</sub>) in such a manner that a weakening of the affinity with respect to oxygen takes place. The reaction may proceed as follows:



The oxygen tension is either increased, the gas becoming more loosely attached than before or, on the contrary, if the addition substance reacts with the solid phase and therefore contains bound oxygen, the oxygen is held more strongly and its tension drops. (3) The oxidation action of metal oxides, such as cupric oxide, may be increased by additions which assist in loosening oxygen; the effectiveness of the oxides, in decreasing order, is Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub>. It is supposed that the formation of compounds between the sesquioxides and cuprous oxide is an explanation for the function of the catalyst in this case (combustion of NH<sub>3</sub> with Fe<sub>2</sub>O<sub>3</sub>—Bi<sub>2</sub>O<sub>3</sub> catalyst). According to the same principle, the small oxidation action of ceric oxide (CeO<sub>2</sub>) is increased by adding aluminum oxide (mixed crystals are formed between Ce<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>). (4) The decrease in oxygen tension (chromium-iron ore is reduced with greater difficulty than ferrous oxide). The addition of oxides isomorphous with ferrous oxide, such as magnesium oxide or manganese oxide, stabilizes ferrous oxide, nickel oxide, and cobaltous oxide by forming mixed crystals (the action of manganese oxide is greater than that of magnesium oxide which, in turn, is greater than that of calcium oxide). (5) A change in the affinity ratio effected through adsorption. For example, palladium oxide adsorbed on silica gel has a smaller affinity for oxygen than when not adsorbed (higher affinity values are obtained when adsorbed in a melted state on silica gel). The decrease in affinity caused by adsorption is not covered by sintering.

It is presumed that the influence of the above factors is not limited to oxygen alone, but applies as well to systems with mobile sulfur, or mobile carbon, as to those with sulfides, or carbides. As a result of compound formation, antimony trisulfide and bismuth trisulfide are stabilized through heavy metal sulfides, such as cuprous sulfide, lead sulfide, etc. Likewise, copper loosens the carbon in Mn<sub>3</sub>C.

Yander and Pfister<sup>11a</sup> made x-ray investigations of the intermediate states occurring in reactions in the solid phase caused by primary defective crystal formation and observed the formation of a spinel from magnesium oxide and alpha-aluminum oxide (molecular ratio 1 : 1) after heating the mixture to a temperature between 400° and 1200°. The reactions involved

included catalytic decomposition of nitrous oxide and the formation of carbon dioxide by the oxidation of carbon monoxide. At low temperatures changes take place in the surface of magnesium oxide, and the activity of the catalyst depends on the presence of specific centers on the surface. At 800°, the maxima of several properties, such as catalytic activity, hygroscopy, and sorption ability, are obtained and a sudden increase in the apparent activation heats is noted in the decomposition of nitrous oxide. At 920°, the irregular primary reaction skin is converted into a spinel crystal. The x-ray diagram in this temperature interval shows an inverted intensity ratio as in the case of a pure spinel. This ratio is displaced with increasing temperature up to intensities of the spinel to the extent to which the dearranged lattice recovers.

X-ray analysis is a method used by investigators in verifying the relationship between the structure of catalysts and their activity. This method is based on the fact that by using crystallites of sufficiently small size the lines in the Debye diagram become enlarged, and therefore less sharp and more indistinct. Using the Debye diagram and measuring the width of the lines on the photomicrograph, the size of the crystallites may be calculated by applying Sherrer's formula:

$$B = \frac{2\sqrt{\ln 2}}{\pi} \cdot \frac{\lambda}{D \cdot \cos \psi} + b$$

The angular width of the line measured between points, in which the intensity of darkening is equal to half of the maximum darkening of the line  $B$ , is plotted as a function of  $1/\cos \psi$ ;  $D$  is calculated from the inclination of the straight line obtained, which is the length of the edge of the cube, and  $B$  is that part of the line on the ordinate axis which is a function of the thickness and the adsorption ability of the preparation. A more accurate formula by Laue permits a comparison of the enlargement of single lines from which conclusions may be drawn concerning the form of crystallites. However, the enlargement of lines takes place only when the diameter of the particles is less than  $10^{-5}$  to  $10^{-6}$  cm. With particles having a greater diameter, the lines do not show a marked enlargement and the method is not applicable. Only when particles are  $10^{-3}$  cm. in diameter are they visible on an x-ray diagram; otherwise the lines are broken and tend to converge.

Using Sherrer's method described above, many investigators studied the relationship between catalytic activity and size of particles of the catalyst. Wyckoff and Crittenden<sup>414</sup> applied Sherrer's method in studying the effect of activators in inhibiting the growth of iron crystallites in the catalyst used in the synthesis of ammonia. Diagrams of iron catalysts, activated and non-activated and reduced at about 400°, were taken and both showed sharp normal lines. These catalysts were also heated for about four hours in a stream of hydrogen at 650°. Even after several months' use at 450–500°, the activated catalyst did not show a marked growth of crystallites. Clark and Ahorn<sup>79</sup> investigated the activity of platinum catalyst in the oxidation of sulfur dioxide as a function of the size of crystallites and found that the activity does not increase continu-

ously with an increase in the size of crystallites, but passes through a certain maximum.

A further study<sup>80</sup> of the activity of nickel catalyst in hydrogenation and dehydrogenation processes showed that value  $B$  of Sherrer's equation, when plotted as a function of  $1/\cos\psi$ , did not give a straight line, but rather a curve of a third degree equation. Therefore, it was concluded that the size of particles lies beyond the applicability of Sherrer's equation. However, a relationship between the enlargement of lines and the catalytic activity was observed which was contrary to that expected, *i.e.*, the decrease in the width of the lines corresponded to an increase in the catalytic activity. Heardt,<sup>181</sup> employing x-ray analysis, found the following size of particles for metals of the platinum group: platinum black, 4.80 to 11.27 $\mu\mu$ ; palladium black, 4.98 to 11.10 $\mu\mu$ ; rhodium, 2.20 $\mu\mu$ ; iridium, 1.16 $\mu\mu$ ; ruthenium, 1.92 to 3.61 $\mu\mu$ ; osmium, 1.70 to 2.70 $\mu\mu$ .

Taylor, Kistiakowsky and Perry,<sup>379</sup> studying various methods for the preparation of platinum black, showed that samples with smaller sized particles possess greater catalytic activity. Hofmann<sup>183</sup> emphasized the relationship between adsorption ability, catalytic activity and the crystalline structure of carbon, while Hofmann and Lemcke<sup>184</sup> found that natural graphite had much larger crystals and that active carbon samples and activated carbon black were of about the same crystalline structure, though possessing markedly different adsorption properties. The catalytic activity for combining hydrogen and bromine is high in the case of active carbon samples, whereas for carbon black it is much smaller and for natural graphite, still less. The activity of the active carbon samples was increased somewhat by heating in carbon dioxide at 950°; in this manner its effectiveness in promoting benzene decomposition was increased seventeen-fold.

Klar<sup>217</sup> attempted to explain the difference between the adsorption of active centers and the catalytic activity by stating that active adsorption centers have a higher adsorption potential than that of the pure surface. Iron preparations of less activity may be obtained from highly active iron preparations by oxidation and reduction processes or by heating. The active centers may be determined through the adsorption of ethylene, ethane, and hydrogen. The decrease in the activation energy caused by the adsorption of the reaction product corresponds to the potential of the active centers and is determinative with respect to the velocity for the course of the reaction.

An x-ray investigation of the lattice structure and the average size of particles of the layers formed by a cathodic dispersion of platinum, palladium, and nickel on glass plates was carried out by Bredig and Allolio.<sup>63</sup> Alternate layers of platinum and palladium dispersed in ten or more millimeters of hydrogen, when used in the hydrogenation of ethylene, were found to be almost inactive. An x-ray examination, however, showed considerable enlargement of the lattice, indicating a high hydrogen content, which seems to decrease greatly the activity of platinum and palladium, even to destroy it. When dispersed in oxygen, palladium and platinum catalysts form oxide layers which at first are inactive but, by further reduction, become very active. Crystalline nickel, hexagonal in



form, dispersed in hydrogen, when used in the hydrogenation of ethylene, was found to be inactive up to 360°. Catalytically active metals are formed if oxidation is followed by reduction with hydrogen, it being concluded that pure metals themselves are catalytically active substances.

In comparing the x-ray diagrams of pure, solid, catalytically active substances with their inactive form, the first having a density markedly less than the second, it was ascertained<sup>27</sup> that in both cases the position of their lines was identical. However, in the case of active catalysts, these lines were slightly visible, but indistinct. Heating causes an increase in density, as well as an increase in the sharpness of lines, and a decrease in activity. These phenomena may be traced to local disturbances in the crystal lattice which are ascertained by an increase in lattice distances and should represent active centers. A possible relationship between the activation heat and the activity of the catalyst was suggested by Schwab.<sup>326</sup> It is assumed that the surface particles of catalysts may reach a stable energy distribution through a definite temperature of preparation which is maintained on cooling. Therefore, a relationship should exist between the excess energy of active centers, the activation heat, and the activity and temperature in the preparation of catalysts.

Eckell,<sup>107</sup> in his investigations on the various treatments of the surfaces of catalysts and their effect on catalytic activity, as well as chemical conversion, ascertained that: (1) the activity of the non-recrystallized nickel and the polished sheet of nickel cannot be attributed to a change in the available surface, and (2) the treatment in the cold and the effect of polishing influence similarly the structure of the catalyst. In polishing, only the upper atomic layers are disturbed and it is presumed that such an effect on the catalyst layers leads, on the one hand, to a destruction in grain and, on the other hand, to a deformation of the lattice by a hardening of the elastic atoms, especially in the sliding plane and its surrounding region. This hardening is reflected in a strong widening of the x-ray interferences as they are actually observed on the  $K_\alpha$  doublet of the rolled sheet of nickel. On heating, these hardened atoms may be eliminated, this being indicated by a splitting of the  $K_\alpha$  doublet. The activity determinations carried out with nickel preheated at 200°, 235°, 270° and 350° indicate that the decrease in activity is uniform with the splitting up of the  $K_\alpha$  doublet. Eckell believes that his results are conclusive, for he assumes that catalytically active places are distinguished through atoms which have moved in some way from their normal position and have changed atomic distances as well.

Referring to the relationship between the structure of the catalyst and chemical conversion,<sup>108</sup> an x-ray investigation shows that the decrease in activation heat is related to the lattice constant and is the result of the incorporation of aluminum oxide into the ferric oxide lattice. The size of particles ( $3.0\text{--}1.0 \cdot 10^{-6}$ ) determined from x-ray diagrams indicates no relation to the velocity constant ( $K$ ) and the activation heat ( $Q$ ). Although the diagrams of the reflection of electrons seem to indicate a parallel between the velocity constant and the degree of dispersion, according to ( $K$ ) and ( $Q$ ) of Arrhenius' equation there is no relation between activity and dis-

person; rather the favorable action of a decreased activation heat on the velocity constant is offset by a change in  $K_0$ , which is a measure of the conditions of the reaction. The high activity of a catalyst may be due to a greater active surface resulting from either an increase in the total surface, or a decrease in activation heat, which makes possible a course through other intermediate reactions. The relationship between  $K_0$  and  $Q$  shows that both are functions of the energetic state of the surface, while the relationship between  $Q$  and the lattice changes is indicative of the fundamental influence of the steric factor in the catalyst lattice and the catalytic activity.

If the assumption that surface layers play the principal role in catalytic activity<sup>278</sup> is correct, then the reaction mechanism on catalytic surfaces may be viewed as the result of ionization or activation by the surface electrons. The catalytic action of a surface would be, therefore, a function of the maximum kinetic energy of free electrons. If the ionization energy of a reacting molecule located near the catalytic surface becomes smaller than the kinetic energy of certain surface electrons, ionization follows and the molecule is adsorbed.

Nyrop<sup>260</sup> assumes that the adsorbed molecules react with one another like molecules in the gas phase, with a resulting decrease in the activation energy due to ionization and an increase in the number of active collisions between molecules. The formation of new molecules by reaction between adsorbed molecules depends, according to Nyrop, on the relation of various adsorbed molecules to one another and on the ionization energy of the new molecules; the formation of new molecules with highest ionization energy or lowest molecular weight predominates. To a certain extent the formation of new molecules depends also upon the coördination of places of various activity.

Since 1882<sup>114</sup> it has been known that carbon filaments give rise to negative ions and metal strips tend to give off positive ions at low temperatures and negative ions at high temperatures. Thomson<sup>387</sup> in 1899 showed that negative ions liberated from a hot carbon filament at low pressure were electrons and that a progressive increase in temperature and a decrease in pressure increased the ratio of the number of negative ions as compared with the positive ions liberated at the surface of a metal. Thomson's theory<sup>385</sup> takes into consideration the conductivity of metals attributed to the presence of electrons in them. The electric field, when superimposed on the heat motion of these electrons, causes them to move with a definite average velocity in the direction of the potential gradient. This drifting of electrons constitutes an electric current. With an increase in temperature the energy of heat motion of the internal electrons increases and at a certain temperature, characteristic for each metal, it may become sufficiently great to carry the electrons out through the surface of the heated body. In this way electrons are set free and their rate of emission is primarily a function of the nature of the emitting substance, the temperature and pressure of the reaction, the type of surrounding atmosphere, as well as differences in contact potentials.

This property of emitting electrons by heat is not confined to the

list of metal conductors. Haber and Just<sup>177</sup> have shown that when alkali metals, their alloys, or amalgams are attacked by oxygen, hydrogen chloride, phosgene, water vapor, or any other chemically active gases or vapors, electrons are liberated in a considerable amount. Referring to a particular case in which the alloy of potassium or sodium was attacked by carbonyl chloride, Haber and Just estimated that one electron was emitted for every 1600 molecules of salt used. Thomson<sup>388</sup> determined the rate of electrical discharge of various inorganic salts at atmospheric pressure and high temperature and found that oxides discharged only negative ions, chlorides and phosphates, only positive ions, while nitrates gave off both negative and positive ions. The degree of electropositiveness of the metal constituent of salts determines their efficiency in electronic emission. Electronic emission may be due to: (1) a purely thermal increase in the kinetic energy of electrons; (2) the liberation of electrons as one of the products of a chemical reaction, and (3) a photoelectric effect.

Table 1.  
(Garrett,<sup>166a, 156b</sup> Horton<sup>186a</sup>)

Nature of Emission	Pressure	Substance	Temperature (°C.)
Positive	Atmospheric	CaF <sub>2</sub>	297
"	"	AlF <sub>3</sub>	330
"	"	NH <sub>4</sub> NO <sub>3</sub>	312
Negative	"	ZnI <sub>2</sub>	241
"	"	FeCl <sub>3</sub>	355
"	"	NH <sub>4</sub> Cl	352
"	"	CaF <sub>2</sub>	346
"	"	NH <sub>4</sub> NO <sub>3</sub>	342
"	"	MgCl <sub>2</sub>	326
Positive	0.05 mm. CO <sub>2</sub>	AlPO <sub>4</sub>	1100
"	" " H <sub>2</sub>	"	1200
Negative	0.001 mm.	CaI <sub>2</sub>	500
"	" "	SrI <sub>2</sub>	540
"	" "	CaF <sub>2</sub>	600

Experimental evidence points to the fact that chemical action alone is not the direct and immediate cause of the emission of electrons; perhaps electronic emission from alkali metals effected chemically may be considered an exception. Even those investigators who subscribe to the chemical point of view maintain that the electronic emission usually observed may be attributed to the action between the hot metal and the minute traces of residual gas and not to the direct result of a chemical action. In the case of tungsten, all gases acting chemically on the metal were found to decrease instead of increase the electronic emission. Langmuir<sup>227</sup> found that hydrogen caused an enormous reduction in the emission of electrons from tungsten, attributing it to the action of water vapor formed by secondary reactions rather than to the direct action of hydrogen. Attempts have been made to prove that electronic emission can take place as the direct result of a chemical action.

Campetti<sup>73</sup> observed an emission of positive ions when copper combined with oxygen or chlorine, and in determining their mobility was of the opinion that these ions were in all probability composed of cupric

oxide. Klemensiewicz<sup>219</sup> claimed to have observed a similar effect for oxidized copper when reduced in a hydrogen atmosphere. Reboul<sup>1288</sup> assumed that similar results are obtained in the oxidation of amalgamated aluminum and of sodium and potassium by moist air, in the action of hydrogen sulfide on silver and alkali metals, in the action of carbon dioxide on alkalies and of nitrous fumes on copper. Thomson<sup>386, 387</sup> observed an emission of electrons when hydrogen was introduced into an alloy of sodium and potassium. Although the number of electrons is very considerable in comparison with the chemical action taking place, Thomson ascertained that sodium, when immersed in a hydrogen atmosphere, reacted similarly to platinum and palladium, that is, with an increase in the emission of electrons. However, it is believed that hydrogen brings about a change in energy, which accompanies the escape of an electron, as well as a change in the contact potential.

Wilson<sup>407, 408</sup> estimated the work done by an electron passing from the interior to the exterior of a pure metal and found that it includes both that corresponding to the Peltier effect at the interface and the change in energy at the outer surface, and is equivalent to the difference in contact potential. It was postulated by Wilson that the work necessary for the escape of an electron may be attributed to the presence of a double electric layer of thickness  $t$  charged negatively on the outside at the surface of the metal. Since the double layer consists of charges of surface density  $+\sigma$  and separated at distances  $t$ , the work done in carrying a charge  $e$  across the layer is  $4\pi\sigma te$ . According to Wilson,  $\sigma$  and  $t$  are independent of temperature. When hydrogen is present,  $t$  remains unchanged, but it may effect a reduction in the value  $\sigma$ . It is supposed that variation in work with temperature may be caused by a diffusion of electrons into the surface layer due to their heat movement. This diffusion of electrons increases with an increase in temperature and increases the effective strength of the double layer. However, diffusion is greater at a given temperature the smaller the value of  $\sigma$ , and when hydrogen is present, the temperature coefficient is greater than in its absence. If the catalytic activity of a substance used as a catalyst is considered with regard to the number of electrons emitted, then the first requisite for the collision of free electrons with atoms and molecules of the reacting system would be an unfailing source of electrons of low velocity and a reasonably narrow range of velocity distribution.

The electronic emission from an incandescent platinum strip or filament may be increased by coating it with thin layers of: (1) alkaline-earth oxides, such as barium oxide; (2) tungsten; (3) thorium on tungsten; (4) molybdenum; (5) nickel and platinum surfaces coated with caesium, and (6) tungsten and platinum surfaces coated with alkalies or thorium. Frenkel<sup>154</sup> found that the photoelectric threshold of tungsten coated with caesium is less than that of pure caesium, and explained it on the basis of a catalytic effect of tungsten on caesium, the latter being a source of photoelectrons. A decrease in the photoelectric threshold of the pure metal caesium below the ionization potential of the isolated caesium atom may

be attributed to an autocatalytic effect of the metal body on its surface atoms.

An adsorbed caesium atom on a tungsten surface is present as an ion and is regarded as being held to the metal by its image form. The ion tends to draw induction electrons from the metal toward itself. The force between the ion dipoles is given as:  $f = 3/2m^2/r^2$ , where  $m$  is the electron moment of the dipole and  $r$ , the distance between them. The contact potential  $\gamma$  of a metal surface covered with an adsorbed film as compared with that of the bare metal surface is given as:  $\gamma = 2\pi\sigma M$ , where  $\sigma$  is the number of adsorbed atoms per sq. cm. of tungsten surface, and  $M$ , the dipole moment. The electron emission is related to the contact potential by means of the equation:

$$\frac{\gamma_e}{\gamma_w} = \frac{\gamma_e}{CkT}$$

where  $\gamma_w$  is the electron emission from pure tungsten, and  $\gamma_e$ , the electron emission from tungsten with adsorbed material upon it. (These surfaces act as catalysts for the decomposition of ammonia.<sup>46a, 228a, 228b, 379b</sup>)

Tanner<sup>374</sup> and Powell and Brata<sup>281</sup> related the activity of contact catalysts to the emission of electrons or to the presence of streams of ions. Tanner assumed that the electronic emission is influenced by the same thermal conditions which cause catalytic activity. Pietsch<sup>275</sup> approached the problem of catalytic activity of solid bodies serving as catalysts by considering active centers as having special, loose electron couplings which may cause the prevailing energetic behavior. Another contributing factor to energetic behavior is the fact that loose electronic coupling is characteristic of intermediate stages catalytically active.

The atoms of a metal (mercury) vapor may be raised to an excited state, rich in energy, by subjecting it to the action of light of a definite wave length. In the presence of foreign gases the excited metal atoms lose their energy upon colliding with those gas molecules, whereby the latter are chemically changed. Frank and Cario actually proved that in hydrogen at a very low pressure (a few hundredths millimeter of mercury) such excited mercury atoms produce hydrogen atoms. When the primarily formed atoms or radicals encounter foreign gases, they yield most diverse conversions difficult to bring about in any other way.

The function of a catalyst may be to relieve restraints on energy transfer by providing a perturbation between systems otherwise rather isolated. Ions have been considered especially effective for this purpose. Brewer<sup>65a</sup> attempted to correlate ion formation with surface catalysis. According to Brewer's conception the adsorbed gas ions, which he calls "adions," are detected by measuring the change produced in the work function for electrons and by an enhancement of the positive thermion current. The ion or electron escaping from a conducting surface produces work against its electrostatic image attraction. The presence of adions has the tendency to decrease the work function for electrons by counteracting the image field. The experimental results obtained from measurements of the enhancement of the photoelectric emissivity indicate that the

work function varies from point to point over the surfaces, and that the field about the adion is appreciable to about ten times the ion radius.

Brewer<sup>65a</sup> has shown that the number of adions escaping from one sq. cm. of surface per sec. may be expressed by:

$$N = n \sqrt{\frac{KT}{2\pi m}} e^{-mW\phi^2/2KT}$$

where  $n$  is the ion density at the surface;  $K$ , Boltzman's constant;  $m$ , the mass of the ion, and  $W$ , the velocity component an ion must have normal to the surface in order to overcome surface attraction.

According to Brewer, the positive ion current may be expressed also by another equation:

$$N = n \cdot AT^{0.5} \cdot e^{\frac{-e\theta}{KT}} = AT^{0.5} \cdot e^{-b/T}$$

if it is considered that  $0.5mW\phi^2$  expresses work and may be replaced by  $e\theta$ , where  $e$  is the charge on the ion and  $\theta$  is the work function in volts, and  $b$ , Richardson's work function.

If the chemical activity at a given surface is a function of the concentration of ions initiating the reaction then, from the foregoing equation, the rate per unit volume may be expressed as follows:

$$\frac{dp}{dt} = nAT^{0.5} \cdot e^{\frac{-e\theta'}{KT}}$$

where  $e\theta$  is the work necessary to loosen the ions from the surface so that a reaction may take place; therefore  $e\theta'$  is assumed to be the chemical work function and identical with  $Q$ , the energy of activation in the expression for the rate of the reaction. According to Brewer, the fact that  $\theta'$  for chemical action is smaller than  $\theta$  for thermoionic emission suggests that the reaction may occur if the ion is not displaced to an appreciable distance from the surface. Brewer's investigations pointed out that the values of the work function are in line with the concept that chemical activity is dependent on ion formation.

#### METHODS FOR MEASURING THE ACTIVITY OF A CATALYST

Attempts have been made to estimate the "effective activity" of a catalyst. It has been postulated that if the velocity constant is directly proportional to the concentration of the catalyst, the "effective activity" is expressed by the ratio of these two values. Ostwald,<sup>263</sup> studying the hydrolysis of methyl acetate, proposed a method whereby he determined the reaction constant as 0.0055 and the mass of the catalyst (hydrochloric acid) per liter as 12, assuming, for convenience, that the acid itself, rather than the products of ionic dissociation, acts as a catalyst, the activity of which is expressed as follows:

$$\frac{K}{m} = \frac{0.0055}{12} = 0.00045$$

Bredig and Ikeda,<sup>66</sup> studying the decomposition of hydrogen peroxide

by colloidal platinum (0.0055 g./liter), found  $K = 0.0435$  and expressed the activity of platinum as

$$\frac{0.0435}{0.0055} = 7.9$$

The activity of a catalyst may be expressed by the rate of production of a given product per unit weight of the catalyst. This ratio has been termed the "activity number." Rideal and Taylor<sup>293</sup> expressed the activity of platinum gauze serving as a catalyst in the catalytic oxidation of ammonia to nitric acid as follows:

$$A_{\text{Pt}} = \frac{700 \times 1000}{40 \times 24 \times 60} = 12$$

where 700 kg. of nitric acid were obtained from one square foot of platinum gauze, a square foot corresponding to 40 g. of the metal when constructed of wire 0.0026 inch in diameter with 80 meshes to the linear inch. Where the catalyst applied is of a definite geometrical form, *i.e.*, plate, foil, or wire, the activity is expressed as the rate of production per unit area of the catalyst. If the rate of production is not constant, comparable results may be obtained by dividing the reaction constant by the area of the catalyst.

Bredig and Teletoff<sup>65</sup> found that a platinized platinum foil 20 sq. cm. in area gave a unimolecular reaction constant of 0.0094 in the decomposition of 900 cc. of hydrogen peroxide (0.3 g. mols of hydrogen peroxide per liter) and estimated from this that the activity of the platinum foil was:

$$A_{\text{Pt}} = \frac{0.0094}{20} = 0.00047$$

Haber and Greenwood<sup>176</sup> proposed the factor space/time yield as corresponding to the activity number. This factor states the volume of product produced per hour per unit volume of catalyst. Table 2 shows the effect of space velocity of the reactants on the composition of the exit gas and on the volumes of product produced per unit time per unit volume of the catalyst. Volumes of gases are expressed at standard conditions of temperature and pressure and the hour is used as the unit of time. The latter gives data on the synthesis of ammonia at a temperature of 515° and 114 atmospheres' pressure, using uranium carbide as a catalyst.

Table 2.

Space-Velocity of Gas 10 <sup>3</sup> x	% of Ammonia in Flow of Gas	Space/Time Yield
5.2	7.63	0.28
28.5	6.42	1.3
74.4	4.78	2.5
174.9	4.18	5.2

Assuming Bodenstein's theory to apply to heterogeneous catalysis and considering Hofmann's viewpoints on activation conditions, Remy<sup>288</sup> proposed a relationship between the activity of the catalyst and its chemical nature. Comparative investigations on the activity of contact substances

indicate, according to Remy, that predetermination of the activity of the catalyst would be possible if the affinity of metals for oxygen and hydrogen was readily understood. In his tabular presentation of metals of the eighth group of the Periodic System, Remy emphasizes the increasing solubility of hydrogen in this sequence: ruthenium, osmium, platinum, rhodium, cobalt, iron, nickel, iridium, and palladium, and the increasing affinity for oxygen in this sequence: platinum, palladium, iridium, osmium, ruthenium, rhodium, nickel, cobalt, and iron. He postulated that if a metal stands in the first row in a position preceding that in the second then, after pretreatment with hydrogen, it is more active than by an oxygen precharge, and *vice versa*. If a metal stands in the second row in a position preceding that in the first then, in the case of an oxygen precharge, it is more active than with a hydrogen precharge. Comparatively poor catalytic activity is to be expected for metals whose oxides have large heats of formation.

Vallery<sup>399</sup> assumed that the activity of a catalyst may be measured by the activity constant  $K$  of the catalyst which he expressed by the equation:

$$dx/dt = K(a - x)(b - x/2)$$

where  $a$  and  $b$  are the initial concentrations of hydrogen and oxygen respectively in mols and  $x$  the number of oxidized molecules of hydrogen at the moment  $t$ . Coating the catalyst (palladium asbestos) with either antimony hydride or arsenious hydride in a concentration of the order of magnitude  $10^{-5}$  does not show any poisoning effect. The best results—a stable catalytic action for comparing  $\log K$  of various experiments—were obtained after ten minutes. Mark<sup>244a</sup> compared the catalytic activity of equally fine dispersed nickel, platinum and palladium, which he considered chiefly energetic, and proposed the following equation:

$$\Phi = RT \frac{\ln C_k}{\ln C}$$

where  $C_k$  is the velocity of the catalyzed reaction and  $C$  the velocity of the non-catalyzed reaction.

Roginsky and Schultz,<sup>300</sup> studying the decomposition of potassium permanganate with various catalysts, found that by a constant low temperature the position of catalysts in the catalytic activity row remains the same as in the case of a continuous slow increase in temperature; but, if the experiments are conducted at high temperature, the order of catalytic activity is completely changed. Nickel oxide is usually a better catalyst than manganese dioxide; manganese dioxide is better than cupric oxide, and cupric oxide is better than aluminum oxide. When a sufficiently high temperature or a very rapid heating is employed, the order of the catalytic activity is shown as indicated in Figure 1.

A similar effect was observed by Roginsky and Schultz in the decomposition of ammonium dichromate; they attributed the reverse order of the catalytic action to the exothermic character of the reaction and to the influence of the heat capacity of the catalyst. At low temperatures and low velocities of decomposition, the temperature within the decomposed



mixture varies slightly from the temperature of the heating mechanism, and in the presence of a catalyst the catalytic action is proportional to the area of the contact surface of the decomposed substance. At high temperatures and high velocities of decomposition, there is no time for equalization of temperature, the influence of the heat capacity of the catalyst being accounted for otherwise. However, at sufficiently high velocities the influence of the latter factor may become of major importance. The heat capacity of the catalyst is directly proportional to the decomposition veloc-

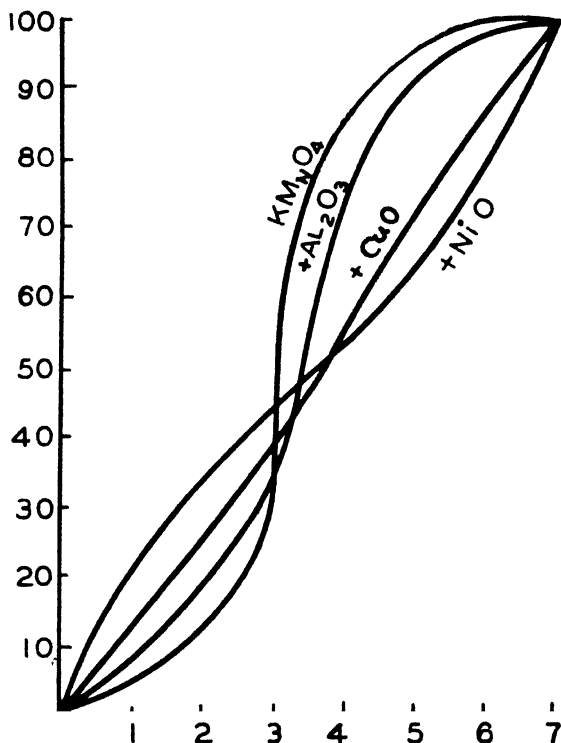


FIGURE 1.

ity and the heat effect of the reaction, and indirectly proportional to the heat capacity of the reaction mixture. The heat capacity of a catalyst is effected in two opposite directions, namely, it increases the velocity of the reaction and increases the heat capacity of the catalyst. Therefore, the reverse order of activity is made possible at the same temperatures at which thermal decomposition in itself has a sufficient velocity. An increase in temperature greatly increases the value of the reaction velocity, since an increase in the heat capacity is related to the velocity of giving off heat which necessarily must increase with an increase in temperature. Since heat evolved by the catalyst causes a further increase in the reaction velocity, the latter in turn increases it too. Therefore the most favorable reaction condition obtainable is one in which a salt without a catalyst is

used, for the temperature at the beginning of a reaction is at its maximum as are also the reaction velocity, self-acceleration and self-heating, which eliminate any unfavorable action of the catalyst. Thus is explained the reverse order of the activity of catalysts, which takes place at the end and not in the beginning of an experiment.

As shown in Figure 1, mixtures with weak catalysts decompose before mixtures with strong catalysts, but mixtures with strong catalysts decompose completely before mixtures with weak catalysts. The more rapid decomposition at high temperature of salts containing a small amount of catalyst may be explained, according to Roginsky and Schultz, by the character of the change in the heat capacity of the catalyst, and by the contact surface of the solid catalyst, with the substance decomposed, which is a function of the amount of catalyst used. Roginsky and Schultz postulated that the heat capacity  $C$  is a linear function of the amount of catalyst used and the amount of substance to be decomposed; therefore

$$C = C_{\text{decomp.}} + C_k M_k$$

where  $C_{\text{decomp.}}$  is the heat capacity of the weighed decomposed substance;  $C_k$ , the specific heat capacity of the catalyst, and  $M_k$  the amount of the catalyst. In the meantime, the increase in the number of contacts made between crystals of the catalyst with crystals of the substance decomposed is slower than the increase in the amount of the catalyst; the slower the increase the greater the content of the catalyst in the mixture. Therefore, the activity or use of the catalyst may be characterized by the ratio of the number of contacts of its points with those of the substance decomposed to the total number of contacts,

$$C_{\text{decomp.}} \cdot \frac{A_{pk}}{A_k} = \frac{M_p}{M_p + M_k \frac{d_p}{d_k}}$$

where  $A_{pk}$  is the number of contacts of the catalyst with the substance decomposed;  $A_k$ , the total number of contacts of the catalyst with its crystals and crystals of the decomposed substance;  $M_p$  ( $p$  = product) and  $M_k$  ( $k$  = catalyst), the mass of decomposed substance and catalyst, respectively, and  $d_p$  and  $d_k$ , their respective specific gravities. In case  $M_p = 1$ , then

$$\frac{A_{pk}}{A_k} = \frac{1}{1 + M_k C}$$

where  $C$  is a constant of the ratio of densities. Thus the retarding action on the heat capacity increases more rapidly than the accelerating action. Under conditions of strong self-heating of the mixture the presence of a large amount of catalyst is a disadvantage, and the addition of catalysts beyond a certain limit not only decreases the catalytic action but retards the reaction as well.

Bowden<sup>61</sup> attempted to define the active surface space in contact catalysis by comparing two methods for measuring the active surface, namely, the electrolytic method which accounts for surface atoms<sup>62a</sup> and the interference method which refers to a surface layer several thousand atoms in

thickness. Srikantan<sup>354, 355</sup> related atomic energy to catalytic activity. In the atomic weight curve of Biltz, the elements which act catalytically are located at maximum peaks. Therefore, according to Srikantan, a function containing atomic weights and vibration numbers may serve as a measure of catalytic activity and is expressed by  $4m^2V/r^2$ , where  $m$  is the atomic weight;  $V$ , the vibration number, and  $r$ , the amplitude of vibrations of atoms calculated from the atomic volume (Lindemann). In the case of noble metals (gold, silver, platinum, and palladium) and carbon used as catalysts, the value of this function is over 100, while for the light ion metals it is below 100.

Pietsch and Seuferling,<sup>277</sup> who considered the fact that the amount of heat set free in most exothermic heterogeneous reactions is returned to the catalyst and is a measure of the activity of the catalyst, determined it by means of a thermo-element, silver Constantan. According to these investigations, the activity of the catalyst as a function of preformation

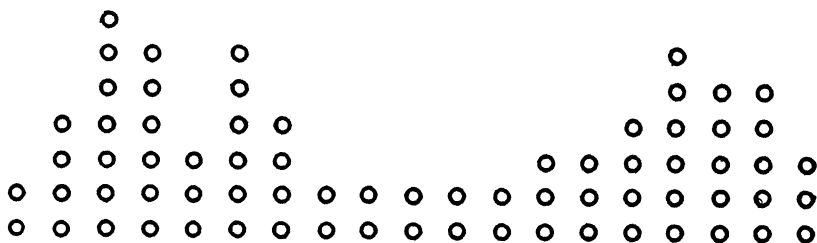


FIGURE 2.—Diagrammatic Representation of the Surface of a Catalyst.

(powder, grain), temperature (additional heating of the catalyst) and ageing and altering, may be calculated to within the limit of error for the activity of a single catalyst aggregate or 0.1–0.5 per cent and for a single series of catalysts, 1.0–4.0 per cent. The less saturated atoms, as well as molecules, possess the greatest binding force in adsorption and the greatest reaction ability in catalysis. Every catalytically active surface has places of different activity (Figure 2). In general, the smaller the number of neighbor atoms the greater the catalytic activity. When the surface of a catalyst is considered spatially, it may be assumed that the surface atoms have from one to 23 neighbor atoms, the top atom with only one neighbor atom being the most catalytically active. On the other hand, the activity of a catalyst is based essentially on the irregularities of the surface (active places, crystal edges, *et al.*).

Steacie and Elkin,<sup>365</sup> in their comparison of the catalytic activity of liquid and solid surfaces of zinc serving as catalysts in the decomposition of methanol, pointed out that if the above viewpoint is correct, the melting of the catalyst should decrease its activity. In measuring the dependence of the decomposition velocity on the temperature of methanol vapor over a constant zinc surface, that is, 0.5 sq. cm. between 360° and 440°, and assuming as a measure of catalytic activity the time within which the total pressure increases by a definite ratio expressed in per cent, Steacie and Elkin found a steady increase in the activity, detecting no variability at

the melting point, or  $420^\circ$ . From this they assumed that the surface of zinc is homogeneously active and that the catalytic activity of a solid substance in general cannot be ascribed to a limited part of its surface. This assumption contradicts the findings of a series of investigations<sup>150, 217, 243, 327</sup> which recognize the fact that no active catalysts may be obtained from a fused mass and that solid active catalysts are prepared by reduction far below the melting or sintering point. As shown schematically in Figure 3, many atoms with a small number of neighbor atoms originate thereby.

It has been stated by Frankenburger<sup>151</sup> that an important factor in the activity of catalysts, in addition to the steric arrangement of the reaction components most suitable for catalytic activity, is that the catalysts themselves should have definite atomic distances and should belong to transition elements<sup>178</sup> which have underneath their external shell an electronic

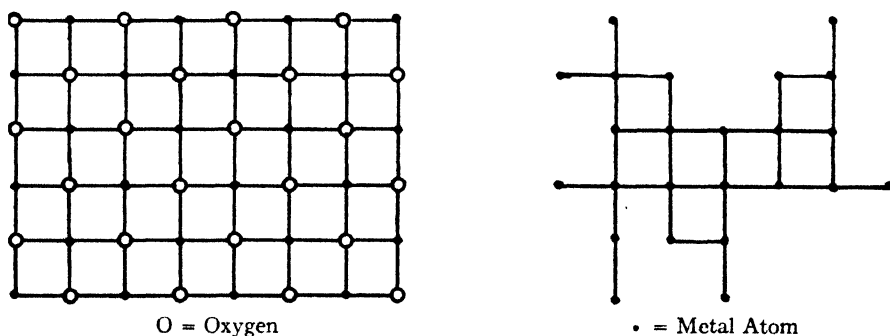


FIGURE 3.—Formation of an Active Metal Catalyst by Reduction of the Oxide below the Melting Point.

level partially occupied and showing a tendency toward electronic exchange. In order to estimate quantitatively the activity of a catalyst, a thorough study should be made regarding the distance relations of atoms, atomic groups and molecules; in other words, the steric arrangement of all components in the catalyzed system. Polanyi and his co-workers<sup>279</sup> attempted to measure these relationships quantitatively.

Boresskow, Guminskaja and Plegunow<sup>56a</sup> describe an apparatus and standard method which they used for measuring the activity of catalysts used in the oxidation of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$ .

Dolch<sup>95</sup> proposed calculating the activity of a catalyst according to thermodynamics, using an isochoric equation:

$$R_k = (C_v^n)/(C_w^n) = R \cdot C^{A/RT}$$

where  $(C_v^n)$  and  $(C_w^n)$  are equilibrium products of the original reacting substances and  $R$  is the actual state of equilibrium. Dolch is of the opinion that if equilibrium relationships were known for all complex reactions, conclusions regarding the activity of a catalyst could be readily drawn and valuable working diagrams obtained.

Schenck<sup>213b</sup> believes that by following gas equilibria over solid surfaces a conclusion may be drawn with respect to their activity relationship. It

has been ascertained that a strong decrease of the particle size in the case of iron makes it essentially less noble. This holds true also for most of the other metals. The possible application of the isothermal equilibrium profile to the investigation of catalysts has been indicated by Schenck in this work.

Thiele<sup>382a</sup> studied the relationship between the catalytic activity and particle size and found that below a definite particle size the catalytic activity of a porous catalyst is proportional to the amount present. With a decided increase in particle size above this limited value, the activity depends on the total external surface. These two regions are separated by the dimensional free value:

$$X_s \sqrt{(C/rK)}$$

where  $X_s$  is the radius of single particles;  $C$ , the activity of the internal surface unit;  $r$ , the hydraulic radius of the pores; and  $K$ , the diffusion coefficient.

#### ACTIVITY AND PREPARATION OF CATALYSTS

**Platinum.**—It is an established fact that the activity of a catalyst greatly depends on the method by which it is prepared, and it is apparent that the conditions under which a catalyst is obtained affect, to a great extent, its physicochemical properties. These properties are the surface and structure of the catalyst and its power to occlude gases. Willstätter<sup>409</sup> related the catalyzing action of platinum and palladium in hydrogenation processes to a transfer of hydrogen concomitant with a de-oxidation due to the simultaneous presence of active oxygen and hydrogen in these metals. Not only is the method of preparing a catalyst important, but its form is just as essential. For instance, the activity of platinum is wholly dependent on the form in which it is used, *i.e.*, whether as a powder, such as platinum black, as sponge, as platinized asbestos, or as platinum wire. Also, the method of preparation determines the degree of dispersion of the catalysts of the platinum group, as well as their activity.<sup>236</sup>

Due consideration has been given to the physical state of the catalysts of the platinum group.<sup>11, 23, 340, 373</sup> In the preparation of platinum black, the most important physical factors to be considered, as stated by Adams, Voorhees and Shriner<sup>6</sup> are: (1) temperature; (2) media in which reduction of platinum oxide proceeds to platinum black, and (3) retarding influences of traces of inorganic salts and spent solvents. Aquirreche's<sup>20</sup> catalytic experiments using platinum oxide showed that not only the velocity at which the hydrogenation of salicylic acid proceeds is influenced by the solvent (therefore the solubility of the substance to be hydrogenated), but the state of the activity of the catalyst as well. He found that if salicylic acid is dissolved in acetic acid the catalytic reaction requires but a few seconds and platinum soon becomes inactive; if it is dissolved in alcohol, catalysis requires a few minutes and the activity of platinum decreases slowly. When hydrogenating salicylic acid in decalene, it was observed that the catalytic reaction required still more time and that it was sufficient to wash the mixture with alcohol in order to dissolve out the excess

salicylic acid; a reactivation of the platinum catalyst followed, due to the fact that it was present in part in a colloidal suspension. This was considered proof of the fact that the activity of a catalyst is dependent on its degree of dispersion. From the corresponding hydrogenation curves it has been deduced that the catalytic reaction reached its maximum at the moment when all of the platinum oxide was reduced; therefore, the activity depends on the presence of metallic platinum.

Taylor, Kistiakowsky and Perry<sup>379</sup> attempted to establish a relationship between the catalytic activity and the method of preparation of three platinum catalysts. These were prepared by: (1) heating ammonium chloroplatinate at 200° in a stream of hydrogen and then subjecting it to a stream of nitrogen at 250–300° for 24 hours; (2) pouring a solution of platinum chloride in formaldehyde into boiling sodium hydroxide and washing the precipitated platinum with hydrochloric acid and water, and (3) reducing a platinum chloride solution with a hydrazine sulfate solution and washing out the chlorine. When subjected to an x-ray examination, the first showed sharp lines on the entire film, while the lines of the second and third were wider and less sharp. The crystals of the first were larger than  $16^{-5}$  cm., while those of the second and third, calculated according to the Debye-Sherrer formula, were of the order of magnitude of 30 Å. The particle size was determined microscopically by sedimentation experiments in castor oil. The particles of the first and third were found to be more coarsely divided ( $0.4 - 4 \times 10^{-4}$  cm.) than those of the second, which were very finely divided (average,  $0.3 \times 10^{-4}$  cm.). In the case of  $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$  and  $2\text{NO} + 5\text{H}_2 \longrightarrow 2\text{NH}_3 + 2\text{H}_2\text{O}$  at ordinary temperature, the sequence of the activity of catalysts for equimolecular mixtures was found to be: third, second, first, while for reactions:  $2\text{CO} + \text{O}_2 \longrightarrow 2\text{CO}_2$  and  $2\text{SO}_2 + \text{O}_2 \longrightarrow 2\text{SO}_3$  at 65–203°, the sequence of the activity of catalyst was found to be: second, third, first.

An oxide of platinum, obtained by fusing chloroplatinic acid with sodium nitrate, has been suggested as an excellent active catalyst for the reduction of organic compounds.<sup>401</sup> In the use of this platinum oxide, the reduction velocity of phenols, pyridine derivatives, aromatic and aliphatic aldehydes, as well as of heterocyclic compounds, is greater than with ordinary platinum black. To a solution of chloroplatinic acid corresponding to 0.9 g. of platinum in 5 cc. of water is added 20 g. of sodium nitrate; the mixture is heated with stirring until the water is driven off, when it is again heated to the melting point, after which it is maintained for from 5 to 15 minutes at a temperature of from 300–320° or until the liberation of brown fumes ceases. The brown precipitate obtained is washed on a funnel with water until no further trace of nitric acid appears in the filtrate.

Instead of chloroplatinic acid, Bruce<sup>70</sup> used ammonium chloroplatinate mixed with ten times its amount of sprayed sodium nitrate and heated the mixture slowly until it melted and a strong uniform gas developed. The melted substance was maintained at 500° for 25 to 30 minutes and the platinum oxide obtained used in the hydrogenation of maleic acid and benzaldehyde.

Tauber<sup>378</sup> attempted to draw a relationship between catalytic activity

and electric potential of platinum and nickel wire, both plated with platinum, which are used in the hydrogenation of ethylene; he found that the change in potential was due to the electrolytic evolution of hydrogen, as well as oxygen, at the end of the metal catalysts. In the case of nickel wire plated with platinum, the reaction velocity was found to depend principally on the pH value of the polarization solution since polarization does not appreciably affect the reaction velocity; the catalytic action of platinum-plated platinum wire was found to be independent of the pH value.

An important role has been ascribed to the hydrogen film originating on the catalyst surface. It has been assumed that smooth, solid platinum and iridium catalysts have an internal surface of great catalytic activity, but that their participation in the activation of hydrogen may cause a decline in their activity. In determining the activation of hydrogen by electrolytically deposited platinum and iridium catalysts through measurements of the polarization of the electrode carrying the catalyst, a loss in the activity of these catalysts in hydrogen at room temperature was ascertained and was related to the activation of hydrogen itself; at high temperatures, the effect was attributed to sintering.<sup>180</sup> The catalytic activity of various films made by the sputtering of platinum on glass receivers has been found to be a function of the nature and pressure of the gas used in the sputtering process and of the potential and duration of the sputtering. Films sputtered in oxygen under conditions which prevent excessive heating of the deposit became active in a  $H_2-O_2$  mixture, but only after the inception of an induction period whose duration was dependent on several factors, in one case being as long as 168 minutes. A study of the electronic diffraction pattern showed that this film, type (A), was composed originally of platinum dioxide and could be converted into type (B) by moderate heating during or after deposition of the metal, producing a film which was immediately active catalytically. Exposing films (A) or (B) to the action of electrolytic hydrogen or to a mixture of  $H_2-O_2$  resulted in a conversion into the active black film, type (C). Drying film (C) for half an hour or heating films (A) or (B) to  $240^\circ$  in air or sputtering them in nitrogen, argon, hydrogen, or oxygen under conditions which keep the receiver hot produced an inactive film, type (D). The electronic diffraction pattern showed that (D) corresponded principally to normal platinum. The development of activity by the yellow film (A) in a stream of  $H_2-O_2$  was observed microscopically and found to be accompanied by the appearance and spread of minute black nuclei. Film (B) formed by sputtering in argon showed a maximum catalytic activity proportional to the thickness of the film, indicating that catalytic action had taken place throughout.

The catalytic activity of thin layers of platinum in the oxidation of sulfur dioxide to sulfur trioxide at  $450^\circ$  was studied by Dankow, Joffe, Kotschetkow and Perewesentzew.<sup>92</sup> These thin layers were obtained by evaporation and condensation of platinum, as well as vanadium pentoxide, on glass, or cathodic dispersion on iron and, in comparison with platinized asbestos, showed very little activity. The decrease in the catalytic activity of thin layers of platinum on glass and iron has been attributed to recrystallization taking place under the conditions of a given experiment.

It also appears that catalysts prepared by the condensation of platinum vapors on asbestos in a vacuum show the same high activity as ordinary platinum on asbestos.

It has been found that the catalytic activity of a platinum gauze increases when used in the oxidation of ammonia; this increase in the activity of a metal catalyst may be attributed to a function of change in the surface structure together with an increase in the true surface of the catalyst; in all probability there are other contributing factors.

Adadurov and Didenko<sup>2</sup> found that a simple thermal treatment of platinum gauze does not effect a structural change in the catalyst, but does influence recrystallization as indicated by x-ray diagrams and, consequently, causes the disappearance of the orientation of the metallic microcrystals. A stable oxide film on a platinum surface interferes with the structural changes in that surface, but when platinum gauze was subjected to a stream of hydrogen for 30 minutes followed by heating to 750° in a stream of nitrogen for 72 hours, no appreciable changes were observed in the oxidation of ammonia; however, treatment in a stream of hydrogen alone resulted in changes similar to those observed in the catalytic oxidation of ammonia. The x-ray diagrams of platinum gauze treated with hydrogen showed a decrease from  $\alpha = 3.903 \text{ \AA}$  to  $3.86 \text{ \AA}$  in the lattice constant. Thereby a solid hydrogen solution with platinum is formed, the melting and sublimation points of which were greatly lowered. When platinum gauze was treated with ammonia or hydrogen at 750°, a loss in platinum was observed and believed to be due to the penetration of hydrogen into the crystal lattice. Adadurov and Didenko concluded that the phenomenon observed, namely, a change in surface structure, increased the activity of the catalyst proceeding parallel to this change, and that the losses in platinum were results of the same process, that is, the removal of the oxide film by a reducing agent, such as hydrogen, and the penetration of that hydrogen into the platinum lattice.

Baker and Co.<sup>30</sup> patented a method for the preparation of platinum contacts which were especially suitable for the oxidation of ammonia. In this method the catalyst consists of a very thin leaf of metal, such as platinum, with small holes punched in it and placed so close together that they form a tooth-like fissure, polygonal in form, and the total surface occupied by this fissure is one-half that of the area of the metal leaf. In another patent<sup>32</sup> it is particularly emphasized that active metals in tissue-like form for use in the combustion of ammonia may be obtained from noble metals of various degrees of hardness. This method serves in the preparation of platinum-rhodium catalysts for which alloys containing various amounts of rhodium are used.

It has been the belief of Zelinsky and Borissow<sup>419</sup> that there are catalysts which are more suitable for hydrogenation than for dehydrogenation processes. These investigators found that a good dehydrogenation catalyst was obtained when 30 g. of active charcoal were stirred with hydrochloroplatinic acid containing 5.2 g. platinum, the solution pipetted off, dried at 100° and then heated in a tube up to 100° in a stream of hydrogen, increasing the temperature after about 2 hours to 140–150°; when reduction



is complete, hydrogen is again passed for one to two hours at 300°, which is the temperature of the dehydrogenation process. This catalyst dehydrogenates methylcyclohexane directly to toluene at 290–300°, but incompletely hydrogenates benzene to cyclohexane at 180°. A similar result has been obtained with platinized asbestos.

Theoretically, according to Packendorff and Leder-Packendorff,<sup>266</sup> any platinum catalyst should hydrogenate as well as dehydrogenate. They succeeded in proving that typical dehydrogenating catalysts show marked hydrogenating characteristics at the optimum temperature (170–180°) for hydrogenation; on the other hand, hydrogenating catalysts convert benzene into cyclohexane to the extent of 30 per cent at 310°.

From the fact that catalysts prepared at 150–180° dehydrogenate very readily and those prepared at 0–10° hydrogenate equally well, an explanation for this behavior is in order. As shown, the activity of a catalyst is less the greater the temperature used in its preparation. Therefore, the ability of a catalyst to dehydrogenate efficiently may be explained by a lesser activity than is required of a hydrogenating catalyst. From this it has been deduced that a typical hydrogenating catalyst may become a dehydrogenating catalyst if its activity is reduced by poisoning.

Packendorff and Leder-Packendorff succeeded in proving that dehydrogenation and hydrogenation catalyses are necessarily dependent on the activity of a catalyst. Substituting Zelinsky's preparation for a platinum catalyst, which is an excellent hydrogenating but a very poor dehydrogenating catalyst, they poisoned it with phosphorus by dropping very rapidly at 310° a dilute solution of phosphorus trichloride in benzene upon the catalyst and passing a stream of hydrogen over it. The catalyst obtained did not hydrogenate benzene even at 220°, but hydrogenated cyclohexane directly to benzene.

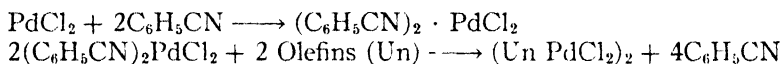
**Palladium.**—The catalytic action of palladium likewise depends on the conditions under which it is prepared and under which catalytic reactions proceed. These conditions may be favorable and promote catalytic activity, or they may be unfavorable and retard it. When palladium sponge is heated in air, the surface of the grayish-white lustrous metal becomes black, due to the formation of the sub-oxide which adsorbs hydrogen very energetically at ordinary temperature and oxidizes to water, causing a heating of the metal.

It has been shown by Hofmann and Zipfel<sup>185</sup> that preliminary treatment of palladium by oxygen increases its catalytic activity from 30 to 50 times. Ruppert<sup>305</sup> stated that the catalytic activity of palladium in hydrogenation and oxidation reactions at ordinary temperature may be increased through a preliminary surface oxidation of the metal, a thin layer of oxygen being deposited. Investigators are also of the opinion that the increase in catalytic activity and in oxidation may be caused by either an anodic polarization or a chemical reaction. The influence of cathodic polarization is rather weak and reflects to an unequal extent in the catalytic action of palladium (or platinum). It has been stated that palladium hydride, when placed in a solution containing hydrogen peroxide or when passing air in water in the presence of palladium hydride, forms a liquid possessing strong

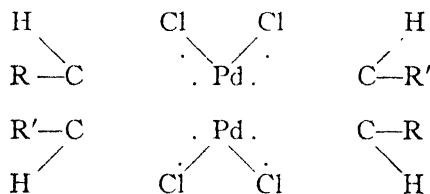
activating properties whose activity is not diminished either in distillation or in filtration or even on standing for many months. No trace of palladium may be detected in the distillate or filtrate.

Fritzman,<sup>155</sup> discussing the catalytic activity of palladium hydride, states that in palladium compounds hydrogen has an unusual valency ( $\text{Pd}_2\text{H}$ ,  $\text{Pd}_3\text{H}_2$ ) due to transition to the metallic state. Metallic hydrides ( $\text{Me}_x\text{H}_y$ ) are similar to organo-metallic compounds or metallic alkides in which the alkyl groups are in combination with the element. The ease with which these compounds decompose and their ability to form addition products makes them especially suitable for use in synthesis and in reduction, and the presence of radicals and hydrogen atoms renders them highly active.

Kharasch, Seyler and Mayo<sup>215a</sup> found that there exist complex compounds of the type (olefin  $\text{PdCl}_2$ ) which they call "coördination compounds." Direct action of ethylene derivatives upon palladium chloride does not lead to the formation of these compounds, but they may be prepared according to the following reaction:



The dibenzonitrilepalladochloride is obtained in a yield 88–95 per cent, if  $\text{PdCl}_2$  and benzonitrile are heated before dissolution is attained. The compound reacts readily with ethylene derivatives in the benzene at room temperature. The precipitation of crystals is favored by the addition of petroleum ether with which they are washed. The crystals are dried over  $\text{CaCl}_2$  at 9–10 mm. pressure. The ethylene compound is prepared by passing ethylene into a benzolic solution of dibenzonitrilepalladochloride, while isobutylene compounds are formed by passing suspended isobutylene into chloroform at  $-78^\circ$ . The compound  $(\text{Un PdCl}_2)_2$ , the structural formula of which is given as follows:



may be obtained with ethylene, isobutylene, cyclohexane, styrene, pinene, camphene, or benzonitrile. However, there may be some doubt as to whether, in the case of cyclohexane, for example, a coördinate compound or a crystalline aggregate is formed.

Palladium, as well as platinum, is often used on carriers. Since the adsorption capacity of the catalyst palladium for hydrogen, as determined under conditions governing catalytic hydrogenation, is dependent principally on the kind of carrier substance used and not on the kind of deposited palladium, the activity of the catalyst depends on how far the palladium compound to be reduced has been adsorbed by the carrier sub-

stance before the reduction occurs and on the degree of distribution of the metal catalyst.<sup>309</sup>

The liquid phase in which the catalyst is distributed during hydrogenation influences its catalytic activity; there is no direct relationship between adsorption capacity and catalytic activity. If the catalytic activity depends on the distribution of palladium on the carrier and in the reaction mixture, and the distribution on the carrier in its turn depends on the adsorption ability of the carrier for the palladium compound subjected to reduction, then an indirect dependence of the catalytic activity on the adsorption capacity of the carrier may be deduced.

Due to its catalytic stability, palladium is very often used in impregnating asbestos.<sup>12, 13</sup> Alexejewsky<sup>10</sup> patented a method for the preparation of a palladium catalyst in which rings are molded from a mixture of kaolin and charcoal and glowed at 950° to render them porous, are then impregnated in the cold with a palladium chloride solution in hydrochloric acid, dried at 100°, and subjected to reduction in a stream of hydrogen saturated with formaldehyde vapors by heating the mass to be reduced in a tubular electric furnace at 100–110°. (The saturation of hydrogen with formaldehyde vapors is carried out by passing a stream of pure hydrogen through a layer of a 40-per cent solution of formaldehyde at room temperature.) Discontinuation of hydrogen chloride vapors liberated from the tube indicates the end of the reduction period and the formation of metallic palladium, which is cooled to room temperature in a stream of hydrogen. The catalyst obtained is dark gray to black in color, uniformly distributed throughout the ring, and said to be active at low temperatures. Palladium oxide comparably active with platinum oxide or platinum black in reduction catalysis is obtained by fusing palladium chloride with sodium nitrate at 600°.<sup>5</sup>

Shukow, Glagolewa and Strukowa<sup>333</sup> compared the catalytic activity of platinum, iridium, rhodium and palladium black in the catalytic decomposition of hydrogen peroxide. The metals were electrolytically precipitated as thin layers on gold, and the velocity constants for the metals per surface unit were found to be practically the same, with the exception of rhodium and palladium black. While rhodium black showed a slightly higher activity than the smooth layer, palladium black underwent decided changes in the process and therefore had little activity; the smooth palladium layer was found to be essentially different from those of other metals of the platinum group.

A method of preparing active palladium catalysts has been suggested.<sup>18</sup> It involves separating the compact palladium metal into single bodies by mechanical means, subjecting the surfaces exposed to chemical purification, charging the single bodies repeatedly with gaseous hydrogen at a temperature below 70° in a ratio corresponding approximately to Pd<sub>3</sub>H<sub>2</sub> by weight, and discharging the adsorbed hydrogen by heating. It is claimed that the palladium catalyst prepared in this manner is very stable, not sensitive to contact poisons, and very suitable in the oxidation of ammonia.

Hercules Powder Co.<sup>182a</sup> suggested the preparation of a platinum catalyst from an alkali solution of the salt by electrolysis. A precipitate of

the complex salt of platinum oxide, such as  $3\text{PtO}_3 \cdot \text{K}_2\text{O}$ , should be formed on the anode which, through treatment with acetic acid, is converted into  $\text{PtO}_3$  and then reduced to Pt.

**Colloidal Platinum, Palladium, and Iron.**—Since the interior of compact metal particles of noble metals does not function in catalysis, it is desirable to decrease it. This may be accomplished by colloiddally dispersing the particles in solution. The practical application of colloidal catalysts has met with difficulty, for only certain types of colloidal metallic solutions are suitable as catalysts. The ordinary methods of preparation give dilute sols which, in a few cases, suffice for active catalysis. The metallic sol must have a concentration sufficiently great to be effective catalytically, and must have a high degree of dispersion. Furthermore, colloids prepared by ordinary methods are very sensitive to electrolytes, especially acids and bases. Thus colloidal catalysts must be prepared with protective colloids, and the protective action of a particular colloid must be sufficient to prevent coagulation under conditions of catalysis; on the other hand, the protective colloid itself must not be poisonous or act as a poisoning agent during the reaction. Sometimes it is necessary to dry the colloidal solution to a gel containing the metal in a state of high concentration, and this gel may be required to be reversibly soluble in water or in an aqueous alcoholic solution so that colloidal solutions of varying concentrations may be prepared. In the case of gum arabic or gelatin as protective colloids, the metallic sols may be prepared in concentrated form without the use of reversible gels.

Paal and Skita have suggested a practical method for the preparation of colloidal metals for use in catalysis. Paal<sup>264</sup> uses as protective colloids the reaction products of albumin, namely, protalbinic and lysalbinic acids in the form of their sodium salts obtained by treatment with sodium hydroxide and sulfuric acid. In so treating, the salt of protalbinic acid is precipitated, while the salt of lysalbinic acid remains in solution. Both are purified by dialysis. These sodium salts are excellent protective colloids as indicated by their gold number which is about 0.05; gelatin ranges from 0.005 to 0.01; and that of gum arabic is about 0.02.

According to Paal, colloidal platinum for use as a catalyst may be prepared by dissolving one gram of sodium lysalbinic acid in 30 cc. water, neutralizing with sodium hydroxide and adding 2 grams chloroplatinous acid dissolved in a small amount of water. Hydrazine hydrate is then added, using somewhat more than its calculated amount (Gutbier). After foaming ceases, the solution is allowed to stand for 5 hours, purified by dialysis, evaporated to dryness on a water bath and dried in a desiccator. The lamellae obtained are slowly soluble in cold water but readily soluble in warm water to which a drop of sodium hydroxide has been added. This preparation contains 50 per cent platinum and 3.5 per cent sodium. An 80-per cent platinum preparation may be obtained by using 0.5 gram of sodium protalbinic acid and 2 grams of chloroplatinous acid.

Paal has prepared colloidal palladium by reduction using either (1) hydrazine hydrate, or (2) molecular hydrogen. In the first case, one part of sodium protalbinic acid is dissolved in 75 parts of water, to which is added

2 to 4 parts of palladious chloride dissolved in 25 parts of water and reduced with hydrazine hydrate in a slightly alkaline solution. After dialyzing and drying, palladium is obtained as a fine, black powder. This 75-per cent palladium preparation loses its solubility in water with time. In the second case, it is recommended to dissolve 1.5 grams of sodium protalbinat in 50 cc. water to which is added sodium hydroxide, taken in an amount more than that equivalent to palladium chloride, and 2.5 grams of palladious chloride in a weak hydrochloric acid solution; reduce with pure hydrogen led into the mixture at 60° for 2 hours. This preparation contains 47 per cent palladium and is claimed not to differ in its properties from that obtained in the first case.

In hydrogenating ethylene, Paal compared the activity of his palladium preparation with that of platinum and found that hydrogenation with palladium sol required only half the time necessary in the case of platinum sol.

Skita's platinum or palladium colloidal solutions for use as catalysts may be distinguished either by their method of preparation or by the type of protective colloid applied. Four classes may be differentiated:

- (1) Noble metals as reversible colloids with respect to water and containing gum arabic as a protective colloid.

- (2) Platinum as a reversible colloid with respect to glacial acetic acid and containing gelatin as a protective colloid.

- (3) Colloidal platinum containing both gum arabic and gelatin as protective colloids.

- (4) Colloidal platinum prepared according to the germ method.

Referring to the first, Skita and Meyer<sup>336, 337, 338</sup> boiled together one gram each of potassium chloroplatinite solution, gum arabic and sodium carbonate in 100 cc. of water with constant stirring for about five minutes, after which it was dialyzed, concentrated on a water bath and dried in a vacuum. The resulting product was dissolved in water in the presence of traces of alkali and the solution shaken with hydrogen until colloidal platinum formed, which was then dried.

Colloidal palladium may be obtained by passing hydrogen under cooling directly into a palladious chloride solution for which an equal amount of gum arabic and sodium carbonate heated to boiling may be substituted; palladium hydroxide first formed is reduced to the metal. In order to avoid the precipitation of finely dispersed metallic palladium instead of the formation of the colloidal solution, it has been suggested adding the unsaturated compound to be catalytically hydrogenated at the beginning of the experiment. Later, Skita prepared colloidal platinum solutions without dialyzing, using hydrazine hydrate as a reducing agent.

Skita determined the amount of protective colloid required from the acidity of the solution in which hydrogenation was carried out. One gram of platinum as chloroplatinous acid was dissolved in 50 cc. water to which was added at room temperature 8 grams gum arabic dissolved in 50 cc. water and the resulting mixture reduced with 25 cc. of a 0.5-per cent hydrazine hydrate solution. This mixture was heated to boiling, cooled to 0°, made alkaline by adding 13 to 15 cc. of a 10-per cent sodium carbonate solution and stirred steadily, heating slightly (one degree increase

per minute). At a temperature between 50° and 60°, a darkening of the solution takes place when it is heated to boiling and boiled for five minutes. Thus the greater part of platinum is reduced to metal and the colloidal solution is applicable as such in hydrogenation processes. If desired, complete reduction of platinum may be effected in 10 to 20 minutes by shaking with pure hydrogen.

The second type of colloidal solution is prepared by dissolving one gram of platinum as chloroplatinous acid in 100 cc. of water and one gram of gelatin in 90 cc. of water, heating each solution separately until boiling and then pouring the gelatin solution not in a boiling state slowly and with continuous stirring into the chloroplatinous acid solution. After cooling, 25 cc. of a 0.5-per cent hydrazine hydrate solution is added to the mixture with stirring and boiled for a short time, the reduction of platinous salt taking place with the formation of nitrogen. This solution is then cooled to 0–5°, 20 cc. of a 10-per cent sodium carbonate solution is added, and the mixture is heated for one hour to 70–80° with stirring until a gradual change in color between temperature intervals of 40–60° is observed. It is then boiled for 5 minutes, cooled and shaken for 15 minutes with hydrogen until no more hydrogen is adsorbed. After dialyzing for 2 days and evaporating in vacuum to about 20 cc., 30–40 cc. of pure 50-per cent acetic acid is added and the solution reduced to 20 cc. in volume, when 50 cc. of the acid is again added and the volume reduced to 20 cc.; finally, a sufficient amount of acetic acid is added to make up 200 cc. of solution.

If two combined protective colloids are used in the preparation of a colloidal platinum catalyst, the procedure is as follows:<sup>336</sup> 1.5 grams of pure gelatin is dissolved in 50 cc. of water and poured into a boiling solution of 4 grams of chloroplatinous acid in 50 cc. acetic acid. After cooling, 25 cc. of a colloidal platinum solution containing 2 grams of platinum and 1.2 grams of gum arabic are added to the first solution. Reduction with hydrogen may be carried out separately or at once in the presence of the substance to be hydrogenated.

The preparation of colloidal platinum as a catalyst by the germ method was described by Skita<sup>337</sup> as follows: Chloroplatinous acid is brought into contact with the substance to be hydrogenated and a small amount of colloidal platinum solution added; sometimes a protective colloid may be supplemented. In using hydrogen or hydrazine hydrate as a reducing agent, the colloidal solution functions as a germ, accelerating its complete conversion into the colloidal state. In this type of reduction it is recommended to increase the temperature slowly and to keep it low in order that the velocity of spontaneous formation of germs may not be exceeded by the increased rate in the velocity of germ growth.

A mechanism according to which colloidal hydrogenating catalysts may function has been proposed by Bourguet,<sup>60</sup> who assumed that in hydrogenation with colloidal palladium stabilized by amidon two compounds are formed,  $\text{Pd}_n\text{H}_2$  and  $(\text{Pd}_n\text{H}_2)\text{A}$  ( $\text{A}$  = the acceptor). Bourguet postulates that in the first stages the reaction velocity is independent of the concentration of the acceptor; therefore the reaction is of zero order, and a change in the activity of the acceptor causes a change in the reaction order. The

first contact between hydrogen and colloidal palladium in aqueous suspension leads to the formation of  $\text{Pd}_n\text{H}_2$ , the particles of which form a homogeneous and oriented layer in the interface of the water-organic phase, whereby  $\text{Pd}_n$  is directed toward water and hydrogen toward the organic phase. The coefficient of agglomeration in the interface is dependent only on the concentration of the metal and hydrogen. Each  $\text{Pd}_n\text{H}_2$  particle attracts only one molecule  $A$  (acceptor); therefore the hydrogen side of the layer is covered with an  $A$  layer. Bonds between  $\text{Pd}_n\text{H}_2$  loosen gradually and the activated  $A$  molecules are set free; thus the catalyst surface is covered with a film of activated  $A$  molecules in equilibrium with the adsorption layer. Activated  $A$  molecules are hydrogenated molecules which may recombine or enter into side reactions.  $A$  is desorbed in the active state and occasionally may recombine or react with hydrogen.

It was ascertained by Rocasolano,<sup>296, 297, 297a</sup> when measuring the velocity of the decomposition of hydrogen peroxide using one and the same sol of palladium or platinum, that the catalytic action first increases, reaches a maximum, and then drops. The reason for such a behavior of colloidal systems in catalysis has been attributed to a change in the concentration of oxygen in the metals. Willstätter and Waldschmidt-Leitz<sup>410</sup> supported this viewpoint, for they also found that palladium black as well as palladium hydrosol hydrogenated only in the presence of small amounts of oxygen; in the absence of oxygen, palladium loses its catalytic property and regains it only when air is introduced. Palladium glowed in an atmosphere of argon was very inactive with respect to hydrogen. Catalyses carried out with colloidal metals are limited to a few reaction types, and the catalytic decomposition of hydrogen peroxide serves as the basis for the kinetics of catalysis with colloids.

Catalytic hydrogenation with colloidal platinum metals has been studied extensively, but catalytic oxidation with colloidal metals has been very little investigated. Schroeter and his co-workers conducted many catalytic hydrogenation experiments using colloidal platinum metals. Investigations on the strength and type of hydrogenation action of colloidal catalysts in hydrogenating unsaturated compounds were of special interest. Wallach,<sup>403</sup> in his study of the terpenes, applied the catalytic hydrogenation of poly bonds to terpenes, using colloidal palladium prepared according to Paal. Skita claims that compounds with double bonds may be hydrogenated efficiently with his colloidal catalyst preparation. Hydrogenation with colloidal platinum metals is considered advantageous over chemical hydrogenation with sodium, sodium amalgam, zinc dust and acetic acid because the reaction may proceed in a neutral solution, thus eliminating rearrangements and/or undesirable conversions of the unsaturated compounds, which are very sensitive to acids and alkalies. Likewise, hydrogenation proceeding at ordinary temperature with metals having highly developed surfaces, such as platinum or palladium black, have a smaller hydrogenation velocity in comparison with colloidal catalysts because the surface of a colloiddally dispersed metal is greater than that of a spongy metal.

Lawrowski, Freiman, Nikolajewa and Putschkow<sup>230a</sup> stated that col-

loidal platinum is subjected much less to a poisoning than platinum black. However, the action of colloidal platinum is greatly weakened by sulfur and arsenic compounds. In the presence of a little sulfur in benzene up to 0.05–0.06 per cent, the aromatics are almost completely hydrogenated and by increasing the amount of platinum, the aromatics may be completely removed. In hydrogenating olefins and aromatics, for example, mixtures of amylene and heptylene with benzene and toluene, these investigators tried to find how far aromatics are attacked in the hydrogenation of olefins. The catalysts used were:  $\text{H}_2\text{PtCl}_6$  + colloidal Pt; colloidal Pt; colloidal Pt reduced with  $\text{H}_2$  before hydrogenation, and  $\text{H}_2\text{PtCl}_6$  + colloidal Pt reduced with  $\text{H}_2$  previous to hydrogenation. It was found that aromatics are the least attacked by using platinum completely reduced in a neutral or an alkali medium. The addition of an acid increases the hydrogenation action in the case of aromatics. Palladium chloride shows no advantage over platinum. Normal olefins of the fatty series are saturated completely by increased hydrogen pressure in the presence of colloidal platinum. Only after saturation of the olefins does a slow hydrogenation of aromatics start. Colloidal platinum reduced in a neutral medium is most suitable for the exceptional hydrogenation of olefins in benzene without attacking the aromatics. In case the hydrogenation is carried out without a solvent (in an aqueous medium) and under normal pressure, the reaction velocity is much too small. In the absence of a solvent, colloidal platinum is likewise unsuitable for carrying out quantitatively the reaction in which  $\text{H}_2\text{PtCl}_6$  + colloidal Pt is used.

The addition of alcohol changes the hydrogenation velocity (with  $\text{H}_2\text{PtCl}_6$ ), but not quantitatively, since hydrogenation of both olefins and aromatics may take place. Colloidal platinum in alcohol shows a definite stop of the reaction at one point corresponding to the olefin content according to the iodine number. In an experiment using 2 cc. of colloidal platinum to 10 cc. of absolute alcohol, and 0.4–0.6 g. of benzene to 20–25 cc. of added hydrogen (pure heptylene (0.1 g.), mixtures of heptylene and benzene, and various benzene fractions), definite hydrogen numbers were obtained for individual olefins.

By hydrogenation of mixtures, the olefins are primarily reduced; after hydrogenation is completed, the hydrogen adsorption stops (duration of the reaction 10–20 min.) corresponding to a hydrogen number of 30.5–33.5; thus hydrogen adsorption continues with a changed velocity. The quantitative hydrogenation of aromatics has been followed in Skita's apparatus using acetic acid solution and high pressure over  $\text{H}_2\text{PtCl}_6$  + colloidal platinum catalyst. The hydrogenation of aromatics from the pyrolysis of benzene was complete at room temperature and three atmospheres pressure. From the hydrogenation curves of olefins-aromatics mixtures, the end of the olefin hydrogenation could be recognized. After hydrogenation of olefins, the aromatics may be determined according to other known methods.

Catalytic practice indicates that colloidal catalysts prepared according to Skita's method should have wider applicability and greater productivity than those of Paal due to the large number of unsaturated compounds which may be hydrogenated; but nevertheless Skita's colloidal catalysts



Table 3. Catalytic Hydrogenation with Colloidal Metals.

Reaction	Catalyst	Remarks	Observer
Hydrogenation of $C_2H_4$ .	Pd sol (Paal). Pt sol.		Paal and Hartmann: <i>Ber.</i> , 42, 2239 (1909). Paal and Schwarz: <i>Ber.</i> , 48, 994 (1915).
Hydrogenation of $C_2H_4$ derivatives, such as fumaric, maleic, and cinnamic acids and their esters.	Pd sol better than Pt sol.		Paal and Gerum: <i>Ber.</i> , 41, 2273 (1908).
Hydrogenation of unsaturated fats.	Pt and Pd sol.	Only in exceptional cases is hydrogenation complete.	Paal and Roth: <i>Ber.</i> , 41, 2282 (1908). Paal: <i>Ber.</i> , 42, 1541 (1909).
Hydrogenation of $C_2H_2$ : $C_2H_2 + H_2 \rightarrow C_2H_4$ $C_2H_4 + H_2 \rightarrow C_2H_6$	Colloidal Pd and Pt. Colloidal Ir and Os do not adsorb $C_2H_2$ .	Pd and Pt (Pd > Pt) prevent to a considerable extent the adsorption of $C_2H_2$ ; the adsorbed $C_2H_2$ does not remain unchanged but is converted into higher molecular compounds surrounding the metals rendering them inactive, <i>i.e.</i> , retard further adsorption and catalytic activity.	Paal and Co-Workers: <i>Ber.</i> , 43, 2684, 2692 (1910); 46, 128 (1913); 48, 1195 (1915).
Hydrogenation of phenylpropionic acid to cinnamic acid: $C_6H_5 \cdot C \equiv C \cdot COOH + H_2$ $\rightarrow C_6H_5 \cdot CH=CH \cdot COOH$	Pt sol.	No adsorption of the acetylene derivatives by the metal sol, therefore no reaction complications.	Paal and Hartmann: <i>Ber.</i> , 42, 3930 (1909).
Hydrogenation of nitrobenzene to aniline using 2 g. nitrobenzene, 10 cc. alcohol and 10 cc. colloidal solution at 80° hydrogenation of benzonitrile and benzaldoxime in water-alcohol solution; reaction products mono- and dibenzylamine: $C_6H_5CH_2NH_2$ and $C_6H_5CH_2NH \cdot CH_2C_6H_5$	Colloidal Cu and Au inactive. Pd more active than Pt and Ir.	Pd sol contained 52.89% Pd. Pt sol contained 57.87% Pt. Ir sol contained 35.00% Ir.	Paal and Gerum: <i>Ber.</i> , 40, 2209 (1907).
Hydrogenation of phenanthraquinone and anthraquinone.	Pt (Skita's, acetic acid and gelatin).		Skita: <i>Ber.</i> , 58, 2685 (1925).
Hydrogenation of nitrobenzene, using 2 g. nitrobenzene, 10 cc. alcohol, and 10 cc. water at 80°.	Hydrosols of: Pd, 0.05 g. Pt, 0.046 g. Ir, 0.05 g.		Paal and Brunjes: <i>Ber.</i> , 40, 2209 (1907).
Hydrogenation of aromatic amines.	Pt (Skita's, acetic acid).	Addition of HCl contributes directly to increase in primary amines.	Skita and Berendt: <i>Ber.</i> , 52, 1519 (1919).
Hydrogenation of substituted phenols, aromatic amines, as well as hydroaromatic ketones and oximes to alcohols and amines.	Colloidal Pt.		Skita: <i>Ann. chim.</i> , 427, 255 (1922); 431, 1 (1923); <i>Ber.</i> , 50, 144 (1922); 51, 1014, 2234 (1923).
Hydrogenation of quinoline.	Pt sol.	10 g. quinoline hydrogenated with 0.7 g. Pt in 9 hours; 30 g. quinoline hydrogenated with 3.0 g. Pt in 2 hours.	Skita and Meyer: <i>Ber.</i> , 45, 3593 (1912). Stepf (Skita): <i>Dissertation</i> , Göttingen, 1927.
Catalytic oxidation of methyl alcohol to formaldehyde.	Colloidal Pt or Cu.		Glässner: <i>Oesterr. Chem. Ztg.</i> , 5, 337 (1902).

Table 3 (Continued).

Reaction	Catalyst	Remarks	Observer
Oxidation of CO to CO <sub>2</sub> .	Pd, Pt, Ir and Os sol suitable.	With Pt sol, 24.3 cc. oxidized to CO <sub>2</sub> in 74 hours (48 cc. CO and 24 cc. O <sub>2</sub> ).	Paal: <i>Ber.</i> , <b>49</b> , 548 (1916).
	Pt black unsuitable.	With Ir sol, 20.0 cc. oxidized to CO <sub>2</sub> in 138 hours (22.65 cc. CO and 24 cc. O <sub>2</sub> ). With Os sol, practically no activity.	
Catalytic oxidation of unsaturated hydrocarbons.	Colloidal Os (prepared according to Makowska: <i>Ber.</i> , <b>41</b> , 943 (1908)).		Willstätter and Sonnenfeld: <i>Ber.</i> , <b>46</b> , 2952 (1915). Wienhaus and Schumm: <i>Ann. chim.</i> , <b>439</b> , 20 (1924). Schmidt, Harry: <i>Dissertation</i> , Göttingen, 1925.
Synthesis of H <sub>2</sub> and O <sub>2</sub> : $O=O+H_2 \rightarrow H-O-O-H$	Traces of colloidal Pt metals.		Hofmann: <i>Ber.</i> , <b>55</b> , 1265 (1922).
Catalysis of detonating gas mixture.	Pd and Pt sol.	Concentration within 1/23-1/5860 N.	Paal and Hartmann: <i>J. prakt. Chem.</i> (2), <b>80</b> , 337 (1909). Paal and Schwarz: <i>Ibid.</i> , <b>93</b> , 106 (1916).
Catalysis of detonating gas mixture; ratio: H <sub>2</sub> : O <sub>2</sub> = 2 : 1.	Pt sol (Bredig's electric dispersion method).	Concentration within 1/5000-1/64000 N.	Ernst: <i>J. Russ. Phys.-Chem.</i> <b>37</b> , 448 (1907).
Decomposition of H <sub>2</sub> O <sub>2</sub> .	Traces of colloidal metals.		Bredig: <i>Z. Elektr.</i> , <b>12</b> , 581 (1906). Teletow: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>39</b> , 1358 (1908).

find little use. Two reasons may account for this, according to Hückel:<sup>193</sup>

(1) Energetic catalysts such as Skita's are not applicable for most synthetic or natural compounds, whereas Paal's or any other non-colloidal catalysts are more suitable; and (2) hydrogenation with Skita's colloidal catalysts requires special equipment and more careful manipulation of the process than when platinum black is used, even though the reaction period is of longer duration; however, it is more suitable for the hydrogenation of smaller amounts of substances without special precautions.

**Nickel.**—That the catalytic activity of nickel is dependent on its method of preparation has been strongly emphasized; sometimes the oxides are more active, sometimes less active, than the metal itself. Likewise, nickel used in catalytic hydrogenation depends for its activity on the reduction temperature of nickel oxide. The surface properties of nickel reducible at different temperatures vary, as indicated by its color. Nickel prepared at 300° is black with a highly developed surface and correspondingly is a very good catalyst, whereas nickel prepared at 500° is gray with a white metallic luster and wholly unsuitable for catalytic purposes.

Brochet,<sup>67</sup> discussing the properties of active nickel used as a catalyst in organic chemistry, states that the pyrophoric property is based only on the occluded hydrogen and that there is no relationship between the pyrophoric property and the catalytic activity; the removal of the pyrophoric property by precipitation maintains catalytic activity and if lost it may be regained to a greater or lesser extent by heating with hydrogen.

Gauger<sup>188</sup> studied the catalytic activity of nickel catalyst prepared by electroplating a tungsten wire with nickel, the electrolyte consisting of nickel sulfate, sodium fluoride and boric acid and the electrode of Kahlbaum's nickel. The wire was sealed in a glass tube connected to another glass tube containing glass (Pyrex) wool and the apparatus glowed and evacuated at 450° for 72 hours. The upper tube containing the wire was held at a temperature above 100° while the lower tube with the glass wool was immersed in liquid air. By sending a strong electric current through the wire, nickel was evaporated and deposited on the glass wool, after which the glass tube was sealed off and used as a reaction vessel. No reaction occurred when hydrogenating ethylene. Negative results were also obtained with platinum catalyst prepared in the same manner. It is Gauger's belief that the activity of a catalyst does not depend so much on the magnitude of its surface as on its preparation, and therefore on the electronic arrangement in the atoms.

Finely divided metallic nickel is a hydrogenating catalyst very suitable for wet, as well as dry, catalytic reduction. The oxides of nickel, however, are considered unsuitable for catalytic reduction by the dry method, but possess an unusual activity in the application of the wet method. This activity is not to be attributed to reduced nickel and was assumed to depend on the oxidation stage. It has been postulated that nickel oxides are advantageous because of the ease and simplicity of their application.<sup>331</sup>

Sabatier and Mailhe<sup>311</sup> considered the catalytic properties of nickel oxide to be comparable to those of finely divided platinum in the oxidation of hydrocarbons. The higher oxides, nickel sesqui-oxide and nickel dioxide, are produced by anodic oxidation or by the action of alkaline hypohalides on the metal or its salts. The active material of positive plates of nickel-iron alkaline accumulators, such as the Edison cell, is composed largely of nickel sesqui-oxide in the charged condition, with an appreciable amount of nickel dioxide when freshly charged. At ordinary temperatures, nickel dioxide is very unstable. In its oxides, nickel possesses unusual characteristics for oxidation catalyses. The most common and the most stable oxide is nickel monoxide, the ease of its reduction to the metallic state depending greatly on the conditions of its initial formation. Sabatier implied that many metal oxides, among them nickel monoxide, are oxidation catalysts because they are readily reduced to the metal or to a lower oxide by the substance catalytically oxidized. Ipatieff<sup>208</sup> emphasized in his book that nickel monoxide should give a maximum hydrogenation velocity because it is an oxide rich in oxygen. If the reduction of nickel oxides by hydrogen does not proceed to the formation of metallic nickel but to the formation of lower oxides, the latter may function in the same way as reduced nickel. Further, in regard to nickel oxide, it must be noted that it retains water with unusual tenacity and, in order to remove it completely, a temperature as high as 300° is required. Dried nickel oxide adsorbs moisture readily, and it has been inferred that the hydrates of nickel monoxide may be of importance in reduction and oxidation reactions of nickel monoxide.

Willstätter and Waldschmidt-Leitz<sup>410</sup> ascertained that nickel catalyst

treated with hydrogen at 350–360° for 3 hours is inactive and reaches an active state only by the action of a gas containing oxygen; however, nickel prepared at 200–220° as well as at 300° is still active. Kelber's results<sup>215</sup> contradict these findings. By using nickel carbonate, he found that the catalyst prepared at 350–360° possessed good catalytic activity, and that that prepared at 300° was slightly more active. The nickel preparation reduced at a lower temperature was less active. Nickel reduced at 350–360°, when shaken with oxygen at 18–20°, adsorbed considerable of the gas and was then found to be wholly inactive. When the oxygen-containing catalyst was heated with hydrogen up to 70–80°, large amounts of it were adsorbed, and when it was re-heated at a certain temperature the catalytic activity was restored. Kelber is of the opinion that inactivation of oxygen was not ascertained by Willstätter and Waldschmidt-Leitz because they determined the activity at 60°, a temperature at which the inactive catalyst regains its activity.

Regarding nickel oxide catalyst in high-pressure hydrogenation, Ipatieff<sup>208</sup> states that nickel oxide obtained from Kahlbaum contains much more nickel than the formula ( $\text{Ni}_2\text{O}_3$ ) calls for (71% of nickel). Reduced nickel is unable to adsorb significant amounts of hydrogen, but when exposed to the air it heats and some of the particles glow. The behavior of nickel sub-oxide in high-pressure reduction is unlike that of nickel oxide. For instance, nickel sub-oxide may be reduced at 172° to metallic nickel in the presence as well as in the absence of benzene, but if first ignited and afterwards used as a catalyst, it loses its ability to hydrogenate benzene at 173° and to be reduced at this temperature by hydrogen alone. By raising the temperature above 200°, the ability of the catalyst to hydrogenate benzene is recovered. The significance of water in catalytic hydrogenation reactions is emphasized.

Concerning the relative influence of oxygen and the necessity for its presence in catalytic hydrogenation processes, two theories have been proposed, one by Bodenstein, the other by Willstätter. According to Bodenstein,<sup>53</sup> the presence of oxygen is unnecessary, the catalytic effect depending on the field of forces of the surface to deform the adsorbed molecule, thereby activating it. Rupert,<sup>306</sup> Rideal,<sup>292</sup> Mitchell and Marschall<sup>249</sup> and Waser<sup>404</sup> assume that the presence of minute amounts of oxygen (from 0.02 per cent up) is necessary for the activation of hydrogen. Boswell<sup>58</sup> considers hydrogenation with nickel possible only when nickel oxide is reduced to the point where an oxide nucleus is surrounded by a metallic layer on the surface of which catalysis takes place. In all probability a number of the properties of finely divided active nickel increase the usefulness of nickel as a catalyst in hydrogenation and dehydrogenation processes. Nickel catalyst occludes hydrogen readily when heated and adsorbs it, as well as the oxides of carbon and gaseous hydrocarbons, to a greater extent than any other metal. This fact no doubt explains why nickel is a "violent" catalyst in reactions involving hydrogen, whereas other metals, such as copper, which do not adsorb hydrogen or other gaseous materials to the same extent as nickel, are only mild hydrogenation catalysts. Apparently, nickel also has the ability to adsorb organic molecules of many substances

other than hydrocarbons as well as to dissociate molecular hydrogen.<sup>287</sup> Activity in hydrogenation and resistance to poisoning depend to a great extent on the conditions of preparation. Supported nickel catalysts are superior in many respects, particularly when suitable inert substances are used and favorable methods of preparation applied.

Eckell<sup>107</sup> obtained evidence that in the hydrogenation of ethylene with nickel foil its catalytic activity may be improved when, instead of being annealed at temperatures between 200° and 300°, it is treated in the cold. He believes that heat treatment destroys, in this case, the catalytic activity by releasing the atoms from abnormal and active distances to normal and less active distances. Temperature increase causes "sintering" and with it goes the readjustment of the abnormal atom distances of high activity resulting in the reduction of catalytic activity. Such an effect is observed with reduced copper and nickel around 200°.<sup>377</sup>

A catalyst especially suitable for the hydrogenation of unsaturated organic compounds is obtained when nickel nitrate is heated with an organic salt of nickel. For example, a solution of nickel in glyceric acid with nickel nitrate, which may be replaced by pumice or clay, is evaporated to dryness and the mixture decomposed by heating in the absence of air. Depending on the proportion of each substance, a catalyst is obtained which contains a metal oxide or a mixture of finely divided metallic nickel and nickel oxide.<sup>383</sup> A catalyst suitable for the reduction and hydrogenation of organic compounds is obtained when a reducible nickel compound, such as nickel formate or nickel dicyandiamidine (dry, paste, or solution), is surrounded with a sufficient amount of a protective substance and then reduced.<sup>411</sup> In the preparation of nickel for catalytic reduction, conducting the reducible nickel over plates arranged in steps and heating electrically is recommended;<sup>321</sup> finely divided nickel is thus obtained.

Drusner and Sieck<sup>100</sup> washed precipitated nickel carbonate to remove all traces of water-soluble substances, mixed it with an inert non-reducible material and reduced the dried mixture in an atmosphere of hydrogen. In another patent, nickel-formo-carbonate was used to prepare nickel catalyst. Freshly precipitated nickel carbonate was heated with an amount of formic acid sufficient to convert it completely into the formate, and dried.<sup>111</sup> Nickel catalyst for use in the hydrogenation of fats is prepared from a dry organic nickel salt heated to a temperature at least ten degrees above that at which reduction takes place.<sup>110</sup> Nickel catalysts for the hydrogenation of fats or fatty acids are prepared from precipitated nickel carbonate or nickel hydroxide reduced superficially to the metal at a low temperature.<sup>48</sup>

Oils are hydrogenated at 180° with an active and stable-in-air nickel catalyst prepared by precipitating a solution of nickel carbonyl with a solution of sodium carbonate to which a small amount of borax has been added, filtering, washing and heating in a stream of hydrogen.<sup>252</sup> By mixing an aqueous solution of a nickel salt with a solution containing either a magnesium or an aluminum salt and precipitating with water glass, a precipitate is obtained which is washed, dried and heated in a stream of hydrogen up to about 300–500° and allowed to cool in another stream of hydrogen; this catalyst must be kept under oil. Hydrogenation takes place

at 150–160°; simultaneously the oil is bleached, its odor removed, and it is rendered tasteless.<sup>168, 169, 170</sup> A method for preparing catalysts of special activity for use in the reduction of fatty acids was described by the Hydrogenation Patent Application Society.<sup>196</sup> Readily reducible inorganic metallic compounds other than the platinum metals, for example, nickel carbonate, are heated under a layer of oil and reducing gases are passed through under pressure; reduction takes place between 200–250°. The preparation of the catalyst may be combined with the hydrogenation of the oil, the oil being substituted by dry nickel carbonate heated up to 230° and highly compressed hydrogen introduced. As soon as reduction is complete, hydrogenation proceeds at a moderate temperature.<sup>196</sup>

Ellis<sup>113</sup> prepared a nickel hydrogenating catalyst from a nickel compound precipitated together with an insoluble sulfate. Feichner<sup>147</sup> prepared an amorphous nickel catalyst for the hydrogenation of organic compounds which is reduced at low temperature to prevent the baking together of particles on the outside so that the particles on the inside remain intact to reduction. The nickel carbonate precipitate obtained is calcined, washed, dried and reduced.<sup>68</sup> Oxides, hydroxides, or soluble, reducible inorganic or organic salts of catalytically active metals are mixed with hydrates containing silicon dioxide or substances containing such, but in larger amounts. The dry mixture is reduced best by heating with hydrogen. Nickel compounds give a very active, stable, readily filtered catalyst, blue in color, suitable for use in the hydrogenation of fats at about 180°. <sup>314</sup>

Thomas,<sup>384</sup> discussing the factors affecting the catalytic activity of nickel when used in hydrogenation, points out that nickel prepared by reduction with carbon at 600° is rendered active, whereas at 650° it becomes practically inactive. These results could have been predicted from the sintering temperature of nickel. A catalytic substance is claimed to be obtained from a nickel salt solution precipitated with zinc, by grinding the mass and separating the precipitated nickel.<sup>290</sup> A nickel catalyst for hydrogenating and bleaching oils and fats has been prepared by using adsorption compounds of silicates of nickel, magnesium, or aluminum, colloiddally precipitated, washed, dried, pulverized, heated up to 300–500° in a stream of hydrogen and cooled in a stream of hydrogen. Russell and Taylor<sup>308</sup> considered the action of nickel catalyst to be due to the presence of unsaturated nickel atoms, and suggested that, in its preparation for catalytic formation of methane and water from carbon dioxide and hydrogen, reduction should take place at the lowest temperature possible in order to insure obtaining the largest number of unsaturated nickel atoms. They found that the addition of thorium to the nickel catalyst produced the same effect because by the formation of nickel-thorium compounds intermediate spaces originated which counteracted the combining of nickel atoms. This addition also increased the surface area, thereby increasing the adsorption ability for the reacting substances and reaction products.

The Badische Anilin und Soda Fabrik<sup>28</sup> patented as an active nickel catalyst a nickel-magnesium alloy cemented together with a colloidal solution of silicic acid at a temperature of 230° and a pressure of 100 atmospheres of carbon monoxide and heated for 72 hours in a stream of hydrogen

at 300°. Thoren<sup>389</sup> studied the activity of nickel catalyst prepared from: (1) nickel nitrate glowed for one hour at about 500°; (2) nickel hydroxide mixed with aluminum hydroxide (Zelinsky); (3) basic nickel carbonate obtained by hot precipitation of nickel nitrate with sodium carbonate and drying the precipitate at 90° for 4 hours (analysis, 2 parts nickel carbonate, 3 parts nickel hydroxide and 11.7 parts water); and (4) pure nickel carbonate. This catalyst serves in the catalytic hydrogenation of ethylene to ethane. The reaction gases in this experiment were heated together with the catalyst in a closed vessel and the pressure recorded as a function of temperature. It has been found that the activity of nickel catalysts increases by leaps with increase in temperature; thus within certain small temperature intervals the temperature coefficient of the reaction system is considerably greater than within the neighboring temperatures. The temperatures at which these small intervals start and the activation temperatures were found to be constant, and independent of the preparation of the nickel catalyst and the type of reaction involved. The value of the increase in nickel catalyst activity as indicated by these temperatures varies and is not reproducible. In testing the activity of a nickel catalyst in the hydrogenation of ethylene prepared from 10 per cent nickel carbonate and 90 per cent powdered water glass, calcined and reduced with hydrogen, Thoren<sup>390</sup> again found various "activation temperatures," in which the activity either increased in comparison with that of the preceding temperature interval, or the gradually decreasing activity began to decrease more strongly than before. These activation temperatures were -18°, and 10, 40, 61, 81, 100, 120, 139, 163°C., and the activation seemed to occur not at once, but extended over a period of time, more time being required for low temperatures. In experiments with decreasing temperature, an unusual decrease in activity took place, which accounted for the change in the catalyst. It has been assumed that activation temperatures may be related to conversion points, but this has not been confirmed for nickel hydrides.

The I. G. Farbenindustrie A.-G.<sup>120</sup> patented a method for the preparation of nickel in a mixture with a metal of the silver or iron group and reduced with hydrogen at 550°. An electrolytic method for the preparation of a stable nickel catalyst deposited on copper or iron for use in the hydrogenation of fats has been proposed by Swizyn.<sup>369</sup> Yki<sup>415, 416</sup> prepared active nickel catalyst by electrolytic corrosion. A nickel catalyst satisfactory for the synthesis of methanol<sup>82</sup> may be prepared by adding 5 g. of nickel formate to a solution containing 50 g. chromium formate in 350 cc. of boiling water to which 150 g. of activated carbon are added. The mixture is then evaporated to dryness, preferably in an open dish. For the conversion of nitrobenzene into aniline, the nickel catalyst is prepared by stirring, at 30-40 atmospheres' hydrogen pressure at 60-80° temperature, from a solution of nickel acetate treated with oxydisiline, neutralized with acetic acid, and the precipitate washed.<sup>123</sup> A mixture of kieselguhr and calcium carbonate combined with finely dispersed nickel is reduced with hydrogen at 100° temperature under about 40 atmospheres' pressure.<sup>121</sup> The experiments of Gibbs and Liander,<sup>168</sup> in which they used dispersed

nickel in the form of aerosols and aerogels prepared by: (1) condensing nickel vapor in the gaseous mixture at the reaction temperature, and (2) decomposing nickel carbonyl in the gaseous mixture at the reaction temperature indicated that little or no activity was evident in catalyzing gaseous mixtures.

Nickel catalyst, prepared by reducing nickel hydroxide obtained by precipitating nickel salts with a substance less in amount than theoretically calculated, has been found suitable for use in the preparation of methane.<sup>42</sup> Another catalyst suggested for the synthesis of methane is one obtained by impregnating pumice with a solution of nickel nitrate with addition of thorium and cerium nitrates, followed by reduction.<sup>165</sup> Nickel oxide precipitated from nickel sulfate and sodium carbonate and reduced on kieselguhr at 400° and 500°, respectively, appeared to show good catalytic activity in the hydrogenation of soybean oil as indicated by its iodine number; reduction at 600° showed very little activity.<sup>405</sup>

Kautsky and Pfannenstiel<sup>128</sup> prepared a suitable nickel hydrogenating catalyst from a nickel salt solution in which the metal is precipitated by a silicon-oxygen compound, the oxygen content of which must be less than that in silicon oxide, for example, siloxene. A method for preparing nickel catalyst by layering the unchanged nucleus of the nickel metal carrier with amorphous nickel has been patented by the Société d'Etudes et d'Exploitation des Matières Organiques.<sup>350</sup> Nickel wire 2 mm. in diameter was subjected at 150° to a stream of chlorine, the external layer of the metal being converted into nickel chloride and the nucleus remaining unchanged. Treatment with gaseous ammonia at the same temperature leads to the formation of volatile ammonium chloride which escapes and the metallic chloride converts into a sponge-like porous metal adhering to the unchanged nickel. Another active nickel catalyst is claimed to be obtained by impregnating carbon-containing substances with a nickel nitrate solution, drying, reducing, and oxidizing at 800°.<sup>43</sup> The Chemische Fabriken A.-G.<sup>78</sup> recommended a method for the preparation of highly active nickel catalysts suitable for reduction processes. Compounds of the metal catalyst are reduced by hydrogen at an initial temperature of 150–250°, the temperature increasing with progress of the reduction reaction until it is within 200–450°. In addition, a gas mixture composed largely of an inert gas with a small amount of hydrogen is introduced at the beginning of the catalytic reduction, the process being continued with a gas mixture having a hydrogen content greater than the first and containing a high percentage of pure hydrogen in the end.

A nickel catalyst used largely in the hydrogenation of fats and in large-scale organic syntheses is prepared from a nickel-aluminum alloy by powdering it, and then leaching out all or part of the aluminum with caustic soda or sodium carbonate solution. This suspension of nickel, as well as the alloy, is marketed under the trade-name "Raney" catalyst.<sup>284, 285</sup> A nickel catalyst adaptable to low-temperature catalysis has been prepared by Covert and Adkins<sup>90, 150a</sup> from a 1:1 nickel-aluminum alloy by dissolving out aluminum with sodium hydroxide. Acetone has been hydrogenated at 23° temperature under 2–3 atmospheres' pressure for 11 hours, the



amount of catalyst used for 74 cc. of acetone being 8 g. Paul and Hilly<sup>289</sup> describe the preparation of Raney's nickel catalyst as follows: Nickel is introduced into melted aluminum, the nickel-aluminum alloy is then cooled, pulverized, and added to a sodium hydroxide solution which is gradually heated to 90–100° until the liberation of hydrogen ceases; the aluminum solution is decanted and then heated until no more hydrogen is liberated. The operation is repeated three times. The precipitate obtained after filtering is well washed and kept under the liquid. This reaction product is not pure nickel, for it still contains some aluminum.

DuPont<sup>101</sup> prepared nickel for the selective hydrogenation of maleic and fumaric acids, isosafrol, anethol, cyclohexene, and others in a similar manner. An aluminum-nickel alloy containing 40–50 per cent of nickel is treated with concentrated sodium hydroxide first cold, then hot until no more hydrogen is evolved, the precipitate washed until the wash water is neutral to litmus, and the pyrophoric nickel catalyst kept either under alcohol or water.

Boomer and Morris<sup>56</sup> claimed that the most active nickel-chromium catalyst is obtained by mutual precipitation of their hydroxides in the form of nickel chromium oxide,  $\text{NiCrO}_4$ . The dehydrating action of chromium is overshadowed by the dehydrating action of nickel; and only by pre-treatment at a glowing temperature of 1000° or by continued use over a long period of time, resulting in a decreased activity of the nickel, is the dehydrating action of chromium made more pronounced. In leading a mixture of alcohol and water vapor at 235–500° over nickel-chromium catalyst of varying composition, this catalyst appears active with respect to the principal reaction and at the same time furthers the activity of side reactions. However, nickel-chromium oxide is an exception because in this case no reaction takes place between the alcohol and the water—only a decomposition of the alcohol.

Nickel chromite of the empirical formula  $\text{Ni}_2\text{Cr}_2\text{O}_5$  prepared by heating and reducing nickel chromate was considered an especially active catalyst in the hydrogenation of oil.<sup>74</sup> For the hydrogenation of acetylene and the solidification of oleic acid, a finely divided nickel catalyst prepared by the precipitation of nickel hydroxide from a nickel salt solution and reduced with hydrogen at 350° was proposed, the precipitate of nickel hydroxide being used in an amount less than theoretically calculated.<sup>44</sup>

The I. G. Farbenindustrie A.-G.<sup>135</sup> patented a nickel catalyst preparation for use in the catalytic reduction or hydrogenation of organic compounds. Nickel, cobalt, or copper or their mixtures are precipitated from an ammonia solution or its salts and treated with hydrogen or hydrogen-containing gases under pressure in the presence or absence of a precipitated carrier. Treatment with an ammonia solution is carried out with hydrogen in the presence of catalytically active metals. For example, 119 parts nickel chloride are dissolved in 600 parts water and 250 parts concentrated ammonia to which is added 15 parts ammonium chloride; 2 parts of finely dispersed nickel and 150 parts of kieselguhr may then be added. This mixture is then heated at 100° in a rotating autoclave under 30–35 atmospheres' hydrogen pressure and the finely divided nickel catalyst pre-

precipitated on the carrier. This catalyst may be used either in a wet or in a dry condition.

A product obtained by converting a soluble nickel salt first into an insoluble nickel compound and then into nickel formate by the addition of formic acid was found to be an active catalyst.<sup>412</sup> For example, from nickel sulfate nickel is precipitated as a carbonate, which is mixed wet or dry with 85-per cent formic acid and dried. A new method for the preparation of oxide catalysts, particularly nickel oxide, for use in the oxidation of carbon monoxide between  $-70$  and  $+150^{\circ}$  has been recommended by Loane.<sup>238</sup> This method consists in preparing oxide catalysts either by the electrolysis of nickel, cobalt, iron, manganese, or copper sulfate solutions with amalgam cathodes and decomposing the amalgam by vacuum distillation, or by converting water-free salts of cobalt, nickel, iron, or copper nitrates dissolved in liquid ammonia with sodium. In both cases the precipitation of pyrophoric metals is followed by slow oxidation.

According to Bennetti and Frazer,<sup>75</sup> highly active nickel and iron carbonyl catalysts may be obtained by incorporating the metals with mercury and distilling off the mercury, at the same time eliminating gases reacting with the metals; a powder-like substance with a large surface is the final product formed. Nickel carbonyl decomposes at ordinary temperature and iron carbonyl at  $110$ – $120^{\circ}$ .

Nickel monoxide, when treated with an ester of silicic acid, such as ethyl orthosilicate, gives an active catalyst.<sup>294</sup> This mixture is granulated, heated and subjected to the action of reducing gases. Nickel monoxide prepared from a nickel nitrate solution by precipitating with sodium hydroxide, drying and glowing of the nickel hydroxide changes its composition and size of crystal structure under the influence of the temperature used in the preparation of the catalyst.<sup>59</sup> Nickel monoxide prepared at low temperature is composed of minute crystals and free from the hydroxide, as ascertained by an x-ray examination. With increasing temperature the particle size increases, and this increase is believed to follow the equation  $\log D = KT + C$ , where  $D$  is the diameter of a crystal;  $T$ , the temperature, and  $K$  and  $C$ , the constants. When nickel monoxide is treated in the cold with a sodium hypochlorite solution, the x-ray investigation of the crystal size appears to indicate that after oxidation one active oxygen atom corresponds to one surface nickel atom. Measurements of the amount of dehydration of nickel monoxide show that hydration is discontinued when about two molecules of water are present for every oxygen atom. Water adsorption on the surface of nickel monoxide, according to the scheme of Boswell and Iler,<sup>59</sup> indicates that the liberation of water by heating proceeds rapidly up to the formation of a monomolecular layer of water, and thereafter under great difficulty.

In preparing nickel catalyst, the sintering effect on the metal must also be considered. There are substances which, when added to the nickel catalyst, may slow down sintering at high temperatures as, for example, aluminum oxide for use with nickel monoxide. E. Fajans,<sup>119</sup> studying the conversion of *para* hydrogen on nickel catalyst, found that the lower the temperature at which sintering of the catalyst began, the

greater its activity. To each sintering temperature corresponds a state of definite surface activity as regards the existing configuration. After 10 minutes' sintering, the catalyst acquires an activity which remains constant even after many hours of heating. It appears that if the temperature is sufficiently high for sintering to take place, an end value will be obtained which is independent of the preparation of the nickel catalyst; this is true whether the reduction takes place at low temperature (high activity) or at high temperature (low activity).

Schwab and Zorn<sup>327</sup> studied the kinetics of ethylene hydrogenation on melting or skeleton catalysts in the temperature range 0–180° and under pressures of 50–250 mm. The catalysts were prepared by boiling alloys having the sum total of the empirical formula NiSi, NiSi<sub>2</sub>, NiAl, and NiAl<sub>2</sub> with sodium hydroxide. The reaction velocity when the catalyst is prepared from NiSi has been explained according to the theory of Langmuir-Hinshelwood as expressed by the equation:

$$-\frac{dp}{dt} = V = \frac{Kp_{H_2} \cdot p \text{ ethylene}}{1 + bp_{H_2} + Cp \text{ ethylene}} = \frac{KWbp_{H_2} \cdot Cp \text{ ethylene}}{1 + bp_{H_2} + Cp \text{ ethylene}}$$

where  $b$  represents the adsorption coefficient of H<sub>2</sub>;  $C$ , the adsorption coefficient of ethylene;  $K$ , the seeming and  $KW$ , the true velocity constant in the adsorbate. The adsorption heats  $\lambda$  H<sub>2</sub> and  $\lambda$  ethylene for catalyst NiSi are:

$$\lambda H_2 = 12.5 \text{ K Cal.} \pm 3 \text{ K Cal.}$$

$$\lambda \text{ ethylene} = 13.7 \text{ K Cal.} \pm 3 \text{ K Cal.}$$

The true activation heat is:

$$Q_w = 18.7 \text{ K Cal.} \pm 1 \text{ K Cal.}$$

The experimental observations indicate that active centers of catalysts are present essentially in the inside of grains and are reachable there through diffusion into pores. The powder diagrams indicate that catalytic activity is parallel with growing sharpness of interference lines and with increasing cloudiness of the diagram.

Taylor and Weiss<sup>379a</sup> emphasized a possible relationship between catalytic activity and the defective lattice of the catalyst. Frey studied Ni-Al alloys. In the Ni-Al system, three phases exist, namely, Ni<sub>3</sub>Al, Ni<sub>2</sub>Al<sub>3</sub>, and NiAl<sub>3</sub>. The NiAl<sub>3</sub> crystal is a surface-centered cube, possessing a superstructure in which the nickel atoms lie in the middle of the cube surfaces and the aluminum atoms at the cube angles. The Ni<sub>3</sub>Al crystal is a body-centered cube with the aluminum atoms at the cube angles and the nickel atoms in the centers of the cube surfaces. It has also been ascertained that when the aluminum content in alloys of the Ni-Al type increases, the number of nickel atoms in the centers of the cube surfaces decreases. If one-third of the initial nickel atoms leave the lattice, the product would have the composition Ni<sub>2</sub>Al<sub>3</sub>, the cubic symmetry would be destroyed, and the crystal would become trigonal. The free places in the lattice are distributed regularly over the planes perpendicular to the trigonal axis. When Ni<sub>2</sub>Al<sub>3</sub> is treated with sodium hydroxide solution,

aluminum can be removed from the lattice without destroying the trigonal symmetry. The trigonal structure is found even for a nickel content of 80 per cent (the nickel content corresponding to the formula  $\text{Ni}_2\text{Al}_3$  is 59.2 per cent). If the alloy is in normal equilibrium, it would consist of two phases belonging to either the  $\text{NiAl}_3$  or the  $\text{Ni}_3\text{Al}$  type. By further treatment with sodium hydroxide, the lattice is destroyed. An alloy containing 95 per cent nickel gives a diagram of the  $\text{Ni}_2\text{Al}_3$  phase, as well as two surface-centered cubic structures. When the alloy has less than 0.5 per cent aluminum, only one surface-centered cubic phase is present. It is believed that the favorable catalytic properties of the Ni-Al alloy are due to empty places in the lattice.

I. G. Farbenindustrie A.-G. (Stöweker)<sup>146a</sup> patented a method for preparing catalytically active, hard, porous, granular and adsorptive masses by subjecting gels or granular precipitates, their dry products (practically free from silicon oxide), or their mixtures, to a strong mechanical agitation in the presence of a sufficient amount of liquid so that a thin, homogeneous paste is formed and this, after molding or pressing, is dried. If irreversible colloids of the second kind are present, treatment without the addition of water or the action of peptizing agents is required. Catalysts treated in this manner have been prepared by precipitating nickel sulfate and magnesium chloride with sodium carbonate, aluminum nitrate with ammonia or ferric chloride, and aluminum chloride with potassium ferrocyanide.

**Cobalt.**—Cobalt as a catalyst is similar in its properties to nickel. Very often its catalytic activity is designated as of the same order of magnitude as nickel, the methods used in the preparation of cobalt applying to both catalysts. Hüttig and Kassler,<sup>195</sup> in their study of the catalytic activity of metallic cobalt prepared from various cobalt hydrates, found that preparations obtained by precipitation have greater activity than those prepared by direct reduction of the oxides; the reduction temperature should not be increased to 1000–1200°, as this decreases to a considerable extent the activity of cobalt preparations.

Rhenania-Runheim Verein Chemischer Fabriken<sup>289</sup> prepared cobalt catalysts from higher hydrated metallic oxides converted into water-free oxides, at high or low temperatures, wet gases being used for the reduction process, or the reduced metallic oxides are treated with water vapor. Oxygen compounds of cobalt, manganese, or chromium, prepared by the decomposition of salts, such as acetates, or by the oxidation of porous metal carriers charged with the oxide, have been suggested as catalysts for the preparation of ketones from carboxyl-free aliphatic compounds.<sup>186</sup>

The catalytic activity of cobalt sub-oxide alone is limited. It is known that two slightly active substances, when mixed wet, mutually increase their activity. This principle has been applied in preparing catalytic active cobalt compounds. By using manganese-cobalt oxyhydrate, the activity was found to be essentially higher than that of each component. A clumping together of particles takes place when mixing suspensions of both oxides, resulting in the formation of a compound with decreased magnetic susceptibility.<sup>247</sup> Active cobalt-manganese and cobalt-thorium

catalysts may be prepared by precipitation with sodium carbonate. For the reduction of these substances a temperature of 350–400° is required and a period of 4–5 hours. These catalysts have proven stable in the synthesis of benzene from water gas; the manganese and thorium content should not exceed 15–18 per cent.<sup>149</sup>

Especially suitable for the oxidation of carbon monoxide to carbon dioxide are catalysts<sup>335</sup> prepared by chlorinating an aqueous solution of cobalt and iron salts and then alkalizing. The precipitate obtained is washed with water and activated by heating up to about 300°. Cobalt catalyst for the oxidation of ammonia is obtained by precipitating a cobalt salt with an amount of an alkaline precipitation agent, for example, ammonium carbonate, so that only a part of the cobalt is precipitated, the precipitate separated from the solution, and the solution used for obtaining the catalyst by converting the cobalt into the nitrate and decomposing by heat.<sup>24</sup> For the oxidation of ammonia, it has been proposed to use as a catalyst a mixture composed of 85 per cent cobaltic oxide and 15 per cent aluminum oxide obtained by heating to remove hydrogen, which results in the clumping of the reacting substances from which the granulated catalyst is obtained.<sup>25</sup>

Oxidation of carbon monoxide by oxygen in a dry gas mixture at a temperature below 20° is said to be carried out effectively over a long period of time with a catalyst prepared by Frazer.<sup>152</sup> In this method compounds of cobalt or nickel are oxidized in the presence of air or water vapor at temperatures slightly below 250°. For example, 211 g. cobaltous nitrate is dissolved in 200 cc. cold water and treated at 10° with 100 g. sodium hydroxide, to which is added 34.5 g. sodium hypochlorite, the precipitate obtained filtered, washed, dried, and heated.

Catalysts obtained by the precipitation of metallic salts with water-soluble precipitating agents are used for the preparation of hydrogen by converting hydrocarbons with water vapor. For example, solutions of nickelous or cobaltous nitrate are treated with manganese, calcium, barium, strontium, or magnesium hydroxides, carbonates, or oxalates, and the precipitate formed washed, dried, pressed and reduced.<sup>104</sup>

Bishop and Co. Platinum Works<sup>52</sup> state in their patent that an almost complete oxidation of ammonia (about 99.2 per cent) to nitrogen oxide (97.5 per cent) may be possible if the catalyst is a tissue-thin wire composed of an alloy of platinum, rhodium and cobalt previously glowed for about 30 minutes at about 2000°F. and washed with hydrochloric acid; the content of cobalt should be greater than that of rhodium. Another method proposed for the preparation of a cobalt catalyst for the oxidation of ammonia is described as follows:<sup>26</sup> 70 parts of impure cobalt is heated with 3.5–5.0 parts of calcium carbonate and 1.7–3.5 parts of calcium fluoride until melted, the metal separated from the slag and converted into cobalto-cobaltic oxide, pulverized to pass through a 100-mesh screen, mixed with coal to the extent of 17–19 per cent of its weight, and the mixture treated with a sugar solution (one part sugar dissolved in 5 parts water) to form a thick paste, using 6 parts sugar solution to every 15 parts cobalto-cobaltic oxide. This paste is then worked up into coarse grains, dried, and then

reduced to a liquid metal, which is covered with a mixture of calcium oxide and calcium fluoride. For every 100 parts of cobalt, 3.5–5.0 parts of calcium oxide and 1.7–3.5 parts of calcium fluoride are used. Reduction is continued with the addition of fresh material. To decrease the carbon content, cobalto-cobaltic oxide is added to the liquid metals; not more than 0.1 per cent carbon should be present. The liquid cobalt is dropped on water to form globules, the metal purified by dissolving in nitric acid, the insoluble substances removed, evaporated to dryness, and the nitrate decomposed by heating up to 400°. By the use of this catalyst, the oxidation of about 9 per cent ammonia-air mixture takes place at 800°.

**Iron.**—It is a fact that the efficacy of a catalyst is shown not only in a high yield of the reaction product, but in other properties as well; and these factors must be considered in the choice of a catalyst. For instance, in the synthesis of ammonia from hydrogen and nitrogen, uranium and osmium both give high yields; but the first, due to its hygroscopic nature, decreases in activity as the absorption of water increases. Therefore, iron-containing impurities and ferro-molybdenum are, for all practical purposes, more convenient catalysts. Likewise, the method of preparing the catalyst determines its efficiency. Iron catalysts suitable for the synthesis of ammonia may be prepared by reduction of the precipitated hydroxide or the previously glowed nitrate. The latter method gives a catalyst more readily adaptable to a possible change in structure, and withstands high temperatures remarkably well. Iron has better contacting facilities at high temperatures than at low temperatures.

In Figure 4, curve I shows the yield of  $\text{NH}_3$  obtained with a glowed iron catalyst and curve II that obtained with a precipitated iron catalyst.<sup>871</sup>

The diffusion velocity of hydrogen in the case of iron, which is similar to that of palladium, may be changed decidedly by preheating. In both cases the law of mass action of diffusion depends only on the velocity. It is difficult to prepare palladium samples that have reproducible diffusion constants. Samples prepared at temperatures as far apart as 300° and 600° and 760 mm. pressure have given the same diffusion velocity with hydrogen. In case iron contacts nitrogen, the diffusion velocity of hydrogen may be ten to fifteen times greater, but heating at high temperature causes the diffusion curves to drop to their former position. For very low velocities, the diffusion isotherms of iron and palladium correspond to the equation  $K_1 = A_1 p^{1.0}$ , while for very high diffusion velocities,  $K_2 = A_2 p^{0.5}$ .<sup>179</sup>

Sabatier and Mailhe<sup>312</sup> stated that ferric oxide prepared by dehydrating the precipitated hydroxide at a temperature below 350° is a much more powerful catalyst for alcohols than that obtained at red heat. Sabatier<sup>310</sup> explains this situation by saying that catalysis is a question of surface area; therefore the amorphous oxides prepared from precipitated hydroxides dehydrated at low temperatures are much more active than crystalline oxides or those which have been sintered, as well as calcined, at red heat. After calcination, a much smaller surface area available for an advanced stage of molecular condensation is frequent. This is particularly true of metallic oxides having low atomic weights, such as aluminum, iron, silicon, and chromium.

An active iron catalyst was prepared by Davis and Yawl<sup>93</sup> by mixing together a solution of ferrous nitrate and ammonium molybdate, heating it to boiling, filtering, washing and drying the precipitate, igniting, and then reducing it. For the synthesis of ammonia, a catalyst is prepared by allowing a metallic salt to act on a complex iron cyanide, such as potassium ferrocyanide or potassium ferricyanide, the product being free of all soluble complex compounds.<sup>259</sup>

Iron-containing contact materials consisting of a natural ore or an iron salt covered with a thin layer of a basic substance, such as alkaline earths or alkali hydrates, carbonates and nitrates, were considered suitable as

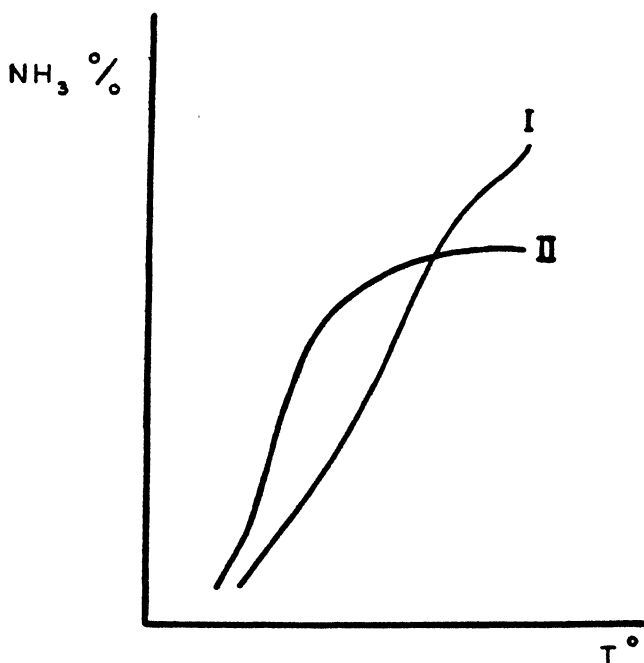


FIGURE 4.

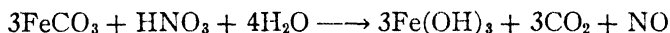
catalysts.<sup>50</sup> Müller<sup>250</sup> used iron carbide as a catalyst in the synthesis of ammonia, and concluded that with pure iron carbide the reaction should proceed below  $450^\circ$ , for at higher temperatures amorphous or colloidal substances, such as metal oxides, hydroxides, or sulfides, must be added in order to prevent the decomposition of the catalyst. The presence of certain compounds, especially cyanides of alkali and alkaline earth metals, greatly improves the action of this catalyst.

A catalyst for the synthesis of ammonia at about  $400^\circ$  temperature and at less than 100 atmospheres' pressure is prepared by mixing together solutions of potassium ferrocyanide and aluminum chloride or aluminum sulfate, evaporating the mixture to dryness in vacuum, reducing the precipitate to powder and treating with pure hydrogen containing nitrogen in a contact space at  $300\text{--}400^\circ$  under pressure.<sup>297</sup>

Rhenania-Runheim Verein Chemischer Fabriken<sup>289</sup> state that contact masses may be prepared by one of two methods, namely, (1) converting the higher hydrated metallic oxides into lower water-free oxides, and (2) reducing the metallic oxides at low temperature or, in the presence of wet gases, at high temperature, and treating the reduced oxides with water vapor. Catalysts obtained from hydrated oxides of iron, cobalt, or vanadium pentoxide are suitable for catalyzing acetylene and ammonia in the formation of nitrogen-containing condensation products. In using the hydrates of iron oxide, the advantages of naturally occurring hydrated oxides, such as brown hematite, must not be overlooked.

Two methods for the preparation of iron catalysts were proposed by Lazote, Inc.<sup>231</sup> In the first, a mixture of the oxides of iron, potassium and magnesium were melted together, ground to a powder, and the mixture filtered; in the second, a solution containing ferrous nitrate and magnesium nitrate was precipitated with an excess of potassium hydroxide, filtered, the precipitate heated to dryness, ground to a powder and reduced with hydrogen or hydrogen-containing gases at 300–700°. These iron catalysts give a yield of 25–30 per cent ammonia in the catalytic synthesis of ammonia at 500°.

Kunsman<sup>224</sup> prepared an iron catalyst by covering platinum wires with a mixture of iron and paraffin, and heating electrically until the iron was oxidized and fused; this was followed by reduction in the presence of hydrogen or hydrogen-nitrogen mixtures. A method for preparing an iron-containing plastic mass for catalytic purposes is described by Dominik.<sup>97</sup> One part of ferrous carbonate suspended in four parts of water is treated with an amount of nitric acid insufficient to convert the carbonate completely into the oxide, sub-oxide, or nitrate, and thoroughly mixed, resulting in the formation of ferric hydroxide according to the equation:



When nitrogen oxide (NO) is exposed to water and air or oxygen, nitric acid forms which again enters into reaction.

That the activity of catalyzing oxides changes, depending on the method and temperature of preparation of the iron catalyst, has been emphasized by Roginsky and Schultz.<sup>300</sup> The activity of iron oxide obtained by thermal decomposition of its oxalate is less than that of nickel monoxide, while iron oxide obtained by decomposition of the sulfate or hydroxide possesses only a moderate activity. Kahlbaum's preparation does not catalyze at all. The difference in catalytic properties in this case corresponds to differences in color, solubility in acids and degree of dispersion, and its activity is less the higher the reaction temperature.

In Figure 5, Roginsky and Schultz show the difference between the decomposition of potassium permanganate with iron oxide catalyst when subjected to 5 hours' drying at 350–370°, dried at low temperature, and glowd, and indicate not only that the grouping of different oxides according to their activity is relative and conditional, but that for each single oxide a definite peak of activity exists and depends on conditions under which the catalyst is prepared.



Littler and Tartar<sup>237a</sup> attempted to test the anodic behavior of iron anodes in sulfuric and nitric acids and that of copper under diminished pressure. As long as the anodes stick out of the solution, they remain active. Iron submerged in nitric acid remains active, also under diminished pressure. Passive iron, however, is not activated through pressure decrease. The pressure minimum at which a passive state takes place was investigated at 25° over a broad nitric acid concentration interval. In sulfuric acid, the iron anodes lose their periodic behavior if the metal is covered with a wax layer on the surface of the liquid. Anodes of iron and nickel in sulfuric acid and of copper in hydrochloric acid and aluminum in nitric acid show a markedly different behavior under diminished pressure if they are provided with a wax layer on the surface of the acid.

The activity of the catalyst depends on a number of factors, such as the structure of the crystalline lattice, the ions composing it, the degree of

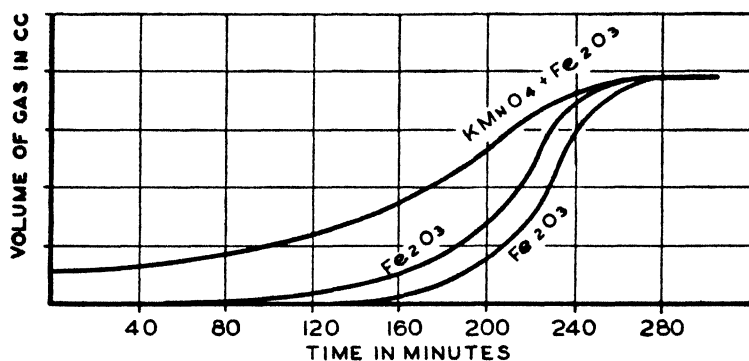


FIGURE 5.

dispersion, the structure of the surface, and its absorptive capacity. In comparing catalysts, their preparation and treatment must be taken into consideration or it must be determined how closely they approach an assumed limit of activity.

The catalytic activity of iron catalyst may be increased by mixing 12 parts ferric oxide with one part aluminum oxide; hydroxides of both metals are precipitated at the same time. A purely mechanical mixing of these components does not markedly change the catalytic action of the ferric oxide.

Hurter<sup>194</sup> prepared an iron catalyst for the synthesis of ammonia by mixing a solution of potassium ferrocyanide with a solution of zirconium chloride, evaporating the mixture and drying the precipitate. After drying, the precipitate is powdered in a hydrogen or a nitrogen-hydrogen atmosphere and heated up to 400° under 90 atmospheres' pressure.

Another method for increasing the activity of iron-containing catalysts was suggested by Glund and Schönfelder,<sup>164</sup> who treated iron with carbon monoxide for the formation of  $\text{Fe}_2\text{C}$  according to the equation:  $2\text{Fe} + 2\text{CO} \longrightarrow \text{Fe}_2\text{C} + \text{CO}_2$ , followed by reduction:  $\text{Fe}_2\text{C} + 2\text{H}_2 \longrightarrow 2\text{Fe} + \text{CH}_4$ . The two catalysts compared were prepared: (1) from melted iron

oxide to which has been added 0.8 per cent of aluminum filings and 1.0 per cent of potassium oxalate (1.5 per cent of aluminum oxide and 0.5 per cent of potassium oxide) and reduced with a nitrogen-hydrogen mixture (the maximum yield of ammonia at 380° was 0.45 per cent); and (2) the precipitated catalyst was washed with pure nitrogen, treated with carbon monoxide at 200–230° so long as iron carbide formed and reduced with a nitrogen-hydrogen mixture until the disappearance of methane (the maximum yield of ammonia at 350° was 0.7 per cent).

The I. G. Farbenindustrie A.-G.<sup>126</sup> prepared a catalyst for the oxidation of hydrocarbons by precipitating a weak acid solution of a neutral metallic salt by a salt of an oxygen-containing inorganic acid to which alkali is added slightly in excess. For example, a mixture of iron and zinc nitrate is precipitated by sodium tetraborate, and this catalyst is treated, before or during use, with a corroding gas, such as hydrogen chloride or nitrosyl chloride.

Seil<sup>328</sup> claimed obtaining ferric oxide by mixing iron and iron-containing products, for example, iron ore, or aniline sludge, with sodium carbonate or potassium carbonate, either dry or in concentrated aqueous solution, and heating for an hour and a half in a rotating oven up to 200–400° or 760–1200°. The reaction product, ferrite, is treated with water and ferric oxide separated by filtration from the alkali solution.

König's method<sup>220</sup> for preparing active iron catalysts takes into account the fact that powder-like metals alone or in mixture with other metals, metal oxides, or carbides may be molded under pressure and sintered in a high-frequency current. For example, finely powdered, chemically pure iron particles are compressed under pressure (100 atmospheres) to pieces one millimeter in thickness. The molded pieces are allowed to fall into a tube enveloped in a cooled copper spiral. An alternating current of 5000 volts per ampere of 500,000 frequency heats the dropping pieces through induction up to 500–600° in an atmosphere of hydrogen, and they are sintered to pressure-stable porous bodies.

In the oxidation of carbon monoxide with water to carbon dioxide and hydrogen, ferric oxide, prepared by pulverizing an oxide of iron to which magnesium oxide has been added and subjecting to heat up to 500–700° under 800–1100 atmospheres' pressure, was considered suitable by Schultze.<sup>325</sup>

Highly active catalysts are prepared by mixing diatomaceous earth or vegetable matter with alkali or alkaline earth compounds to which is added an organic binding material, such as bitumen. Compounds of heavy metals, for example, iron oxide or nickel oxalate, are thinly layered upon this mixture and heated gradually.<sup>255, 256</sup>

For the catalytic oxidation of hydrocarbons, particularly methane, by oxygen, a most efficient catalyst may be prepared from an acidified aqueous solution of a soluble salt of a metal, the oxides of which are difficultly reducible with hydrogen at 600°, or from metals of the iron group treated with an alkali solution of a phosphate or a borate. The precipitate obtained is washed, dried and heated with a small quantity of a gas, such as hydrogen chloride or nitrosyl chloride, either before or during the catalytic reaction.

The conditions under which the catalyst so prepared is used are: to 90 parts of methane and 10 parts of oxygen is added 0.1–0.5 per cent by volume of chlorine; the mixture is heated to 600–700° under ordinary pressure over 0.1 per cent of the highly porous catalyst. The I. G. Farbenindustrie A.-G. also prepared a catalyst from a weakly acid solution of cerium, cadmium and aluminum nitrate taken in equal molecular amounts and precipitated with three times its amount of a secondary alkali phosphate solution containing 100 cc. of an alkali per mol of the phosphate.<sup>127</sup>

Low-boiling hydrocarbons may be prepared by pressure hydrogenation of hydrocarbon oils, tars and phenols in the vapor phase, using an iron catalyst, such as ferroso-ferric oxide, containing a small amount of tin or a metal of the 5th or 6th group, such as molybdenum, vanadium, tungsten or chromium, and reducing with hydrogen. Oxygen is introduced into the melted iron, to which ammonium molybdate or chromium oxide has been added, the mass cooled, and reduced.<sup>199, 200, 201</sup>

Berthou's method<sup>51</sup> for the preparation of metal oxide catalysts, such as iron oxide, having large surfaces, is based on the displacement of certain chemical equilibrium as the result of a selective adsorption of hydroxides by silica gel. Using iron tartrate as an example, there is a possibility of adsorbing hydroxides of heavy metals on silicic acid gels in the presence of ammonium hydroxide.

Schröter<sup>324</sup> states that the synthesis of ammonia or the hydrogenation of carbon monoxide-containing gas may be carried out with a highly reactive iron catalyst obtained by reducing the precipitate resulting from the reaction between ferro-ferric salt solution and alkali.

Catalytic preparation of hydrogen from carbon monoxide and water is favorably carried out with iron oxide obtained by dissolving iron in dilute nitric acid forming ferrous nitrate which is precipitated with ammonia at 60°; the coarse precipitate of the oxide obtained is mixed with a chromate, potassium hydroxide, or clay.<sup>270</sup> In another patent<sup>271</sup> a ferrous salt solution containing potassium dichromate is precipitated with a base and the ferrous hydroxide obtained oxidized by air to ferroso-ferric oxide. The ferroso-ferric oxide precipitate may be formed into a paste by the addition of a potassium dichromate solution.

A stable mass obtained by the action of a strong acid, such as hydrochloric, sulfuric, phosphoric or hydrofluoric, on alkali or alkaline earth salts of ferrocyanide, and evaporated, may be used as a catalyst in the synthesis of ammonia.<sup>342</sup> An aluminum-ferrocyanide compound, insoluble in water and prepared by heating potassium ferrocyanide with aluminum chloride in water, is a good catalyst for the preparation of ammonia at temperatures below 450° in the absence of water vapor. Besides potassium chloride, aluminum-ferrocyanide is obtained after evaporation of water from the precipitate.<sup>343</sup>

A method of preparing catalysts from iron oxide and powdered aluminum, aluminum oxide and iron, or chromium-cerium oxides and iron is based on the principle that non-metallic catalytic compounds may be mixed with a metallic catalytic compound and subjected to pressure, under which the crystals of the metal are deformed, the metal acting as a binding mate-

rial for the original catalytic substances. Such catalysts may be considered suitable not only for the synthesis of ammonia, but for the synthesis of hydrocarbons from carbon monoxide and hydrogen as well.<sup>102</sup>

For the oxidation of carbon monoxide to carbon dioxide, an iron catalyst obtained by the chlorination of an aqueous alkaline solution of cobalt and iron salts was used, the catalyst precipitated being activated by heating up to 300° after washing with water.<sup>335</sup>

Pyrite, after ignition with an oxygen blowpipe to remove any carbon dioxide and sulfur dioxide originally present, was added to iron or other metal of the iron group and the resulting mixture used in the synthesis of ammonia.<sup>302</sup>

Ferrous sulfate treated with ammonia is mixed with chromic acid, and the precipitate dried and pressed. This catalyst serves in the oxidation of carbon monoxide, also in the preparation of methanol and higher alcohols.<sup>103</sup> An alloy containing 90 per cent iron and 10 per cent copper becomes, after surface oxidation, a good catalyst for use in catalytic oxidation.<sup>35</sup>

Preparation of a catalyst for use in the synthesis of ammonia by oxidizing molten iron or an alloy of iron in a stream of oxygen, and heating in a crucible covered with a mass identical with the prepared one,<sup>19</sup> has been suggested. For the conversion of water gas with water vapor at 320–330° a catalyst stable to poisons, such as hydrogen sulfide, is prepared by dissolving 100 kg. iron in dilute nitric acid, treating with 10 kg. chromic acid and 20 kg. potassium chromate, precipitating with ammonia at 60–80°, washing the precipitate, mixing it with 7 kg. barium carbonate and drying.<sup>272</sup> Another active, stable catalyst for the synthesis of ammonia at 550° temperature and 250 atmospheres' pressure [velocity per volume of gaseous reaction mixture ( $3\text{H}_2 + \text{N}_2 \longrightarrow 2\text{NH}_3 \uparrow$ ), and hourly space velocity of reactants = 15,000] is prepared from pure iron or iron-containing ores oxidized in a stream of oxygen with the addition of activators, such as aluminum oxide or potassium nitrate. Keeping the molten liquid continuously under a weak stream of oxygen at a high temperature for some time is recommended. In case an iron ore (magnetite or magnetic oxide of iron) containing a large percentage of impurities (4.0% silicon oxide; 4.2% magnesium oxide; 2.8% aluminum oxide; 0.8% calcium oxide and 0.3% manganese) is used, it is melted by an oxy-acetylene blowpipe, the activators introduced, and the fused mass maintained at a high temperature so that the reaction between iron oxide and activators may run to completion with the elimination of sulfur and phosphorus. In the preparation of catalysts from iron ore, it is advantageous to mix half the amount of activators with the iron oxide, adding the second half in small portions to the partially fused mass. For example, 2 kg. of magnetic oxide of iron are mixed with 50 g. of aluminum oxide and 100 g. of potassium nitrate (added in small portions); the mixture is partially melted, and treated with an excess of oxygen. The catalyst so prepared is discharged and the process repeated.<sup>229</sup>

A catalyst for the synthesis of ammonia under 200 atmospheres' pressure is prepared from iron ore by fine-grinding magnetic oxide of iron,

twice subjecting it to a magnetic separator, partially freeing it from silicon oxide or similar admixtures, and melting after the addition of potassium nitrate or aluminum oxide as activators. The fused mass is pulverized after cooling, again twice subjected to a magnetic separator whereby the silicon oxide content is reduced to 0.3–0.4 per cent, re-melted without the addition of activators, and powdered;<sup>211</sup> the yield of ammonia obtained is 13.5–17.0 per cent under 200 atmospheres' pressure. That the conditions under which reduction takes place influence the catalytic activity of catalysts obtained from natural or artificial magnetite is shown in Table 4.<sup>212</sup>

Table 4. Synthesis of Ammonia (Kamsolkin and Liwschitz).

Pressure (atm.)	Temperature (°C.)	Volume Velocity	Yield (%)
150*	475	15,000	
300†	475‡	15,000	18.5
150*	400	15,000	
300†	450‡	15,000	22.4
150*	450	15,000	
300†	475‡	15,000	16.5

\* Catalyst reduced.

† Tested in catalytic reaction.

‡ Greatest activity.

Mixtures of metals of the iron group are mixed with metals or compounds of difficultly reducible oxides to form a paste, dried, and subjected to a stream of contact gases, such as air, nitrogen, or hydrogen, free from poisons, for 12–72 hours at a temperature of 900–1050°. These catalysts are suitable for the conversion of hydrocarbons by water vapor into hydrogen.<sup>364</sup>

deMahler<sup>244</sup> prepared hydrogenation catalysts, particularly suitable for reduction, from halide salts of iron, nickel, and cobalt by decomposing them with magnesium or zinc in inert organic solvents, for example, low-boiling alcohols, ketones, aldehydes, or ethers. For example, iron catalyst is prepared from hydrated ferric chloride with the addition of magnesium in ether, while nickel catalyst is prepared from hydrated nickel bromide with the addition of zinc dust in ether and slightly heating.

Chlorination of maleic anhydride has been successfully carried out by using one part powdered iron to 100 parts maleic anhydride at 130° and treating with chlorine.<sup>232</sup>

It is claimed by the Amarel Corporation<sup>16</sup> that a catalyst useful in many reactions is obtained by treating Mariel (Cuba) asphalt with superheated steam in a closed retort at 1000–1300° F. under ordinary pressure. The reaction product contains about 85 per cent of iron, (Fe, Al) oxide and silicon oxide, and is especially suitable for the hydrogenation of oil to obtain light hydrocarbons, as well as for the oxidation by air of hydrocarbons to form alcohols, ethers, ketones, terpenes, etc.

The reduction of sulfates, such as sodium sulfate to sodium monosulfide at 600–650° for 3–4 hours was carried out in the presence of an iron catalyst in a mixture with other compounds with a resulting yield of 95–99 per cent. For example, 1000 kg. of sodium sulfate containing

0.2 per cent of iron and 1.5 kg. of antimony pentoxide are thoroughly mixed, wetted with a dilute solution of potassium pyroantimonate, pressed, and dried. To this mixture was added a solution containing 3.88 kg. of copper nitrate and 1.66 kg. of titanium sulfate, and it was then reduced in the presence of 0.6 per cent arsenic trioxide and 0.6 per cent antimony trioxide or 2 parts red lead tetraoxide. With these catalysts, temperatures greater than those indicated above may be necessary for the complete reduction of the sulfates of alkaline earths.<sup>144</sup>

A substance prepared from iron filings about 5 mm. in diameter when treated with 1-per cent acetic acid is covered with an oxide layer and treated with a saturated calcium acetate solution, heated to 500° to decompose the acetate formed and to precipitate the calcium carbonate, has been found to be an active catalyst in the preparation of acetone from alcohol.<sup>31</sup>

Iron fused with activators, such as aluminum oxide and potassium oxide, subjected to the action of ultrasonic waves and treated in the usual manner, was considered a good catalyst for the hydrogenation process and synthesis of ammonia.<sup>356</sup>

A comparison of the catalytic activity of a colloidal solution of iron, prepared from a 2-per cent ferric chloride solution with respect to decomposition of hydrogen peroxide, showed a direct proportionality of velocity constants of the decomposition reaction to the active surface when the dispersity of one colloidal solution exceeded six times that of the other.<sup>382</sup>

Krause and Jankowski<sup>222</sup> considered amorphous *ortho* iron hydroxide as an inorganic oxidizing agent suitable for the quantitative oxidation of acetic acid by hydrogen peroxide. For the complete oxidation of 1/200 *N* acetic acid over 0.2 g. of *ortho* iron hydroxide, 105 hours are required, and for 1/20 *N* acetic acid, about 30 days. The course of the reaction includes the formation of tervalent iron peroxide which dehydrogenates, as well as oxidizes, organic substances, resulting in the re-formation of tervalent iron hydroxide.

Kasarnowski, Borschtschewski and Kosstin<sup>214a</sup> established the possibility of purification of a mixture of  $H_2$ - $N_2$  with carbon monoxide by means of catalytic selective oxidation. To a mixture of  $N_2$ - $H_2$  (prepared from ammonia) was admixed 0.5-0.1 per cent CO and 0.5-1.0 per cent  $O_2$ ; after drying the gas mixture with  $H_2SO_4$  (sp. gr. 1.84) and NaOH, it was led through a contact apparatus containing 5 cc. of a catalyst. The following catalysts were tested: (1)  $Fe_2O_3$ ; (2)  $Fe_2O_3$  + 2.5 per cent of  $Cr_2O_3$  and 0.5 per cent of  $Ce_2O_3$  precipitated on silica gel (30 per cent of the catalyst weight); (3)  $Fe_2O_3$  + 2.5 per cent of  $Cr_2O_3$  and 0.5 per cent of  $Ce_2O_3$ ; (4) Hopcalite (consisting of two or five components: (a) 60 per cent  $MnO_2$ , 40 per cent CuO; (b) 30 per cent CuO, 17 per cent  $Co_2O_3$ , 8 per cent  $Fe_2O_3$ , 6 per cent  $Ag_2O$ ). The Hopcalite catalyst acted best at 100°; 93-95 per cent of CO contained in the gas mixture is oxidized. Above 130° Hopcalite was found to lose its activity and to reduce. The iron catalysts obtained at 230-290° from the mixture  $Fe_2O_3$  with  $Ce_2O_3$  and  $Cr_2O_3$  are favorable. In this case 76-86 per cent CO was oxidized.

**Manganese.**—Oxidation of carbon monoxide, ammonia, sulfur dioxide, aldehydes, alcohols and toluene may be effected at ordinary or at slightly increased temperature by catalysts such as manganese, cobalt, copper, iron, nickel, bismuth, platinum, and silver, prepared by precipitating the metal hydroxides in a state of fine dispersion and drying by heating at a temperature not higher than 250°, or subjecting to a stream of oxygen at 200°. The addition of the platinum group to the dispersed metals greatly increases their activity.<sup>313</sup>

A hydrated manganese dioxide of high catalytic activity is prepared by precipitating a potassium permanganate solution with hydrogen peroxide. In the preparation of the catalyst care is taken that the hydrogen peroxide solution is sufficiently acid to bind the free alkali formed in the conversion. The hydrogen peroxide solution contains the added acid in a very dilute state (a 1-per cent solution) and into this is introduced slowly a 3-4-per cent potassium permanganate solution. The product obtained is free from alkali and very finely dispersed.<sup>98</sup>

A good catalyst for the oxidation of carbon monoxide is prepared from a mixture of bivalent and quadrivalent manganese, the bivalent metal being dissolved out, leaving the quadrivalent metal as a skeleton structure.<sup>203</sup>

**Chromium.**—In general, the difficultly reducible metal oxides catalyze only the hydrogenation of the C=O bond and not the C=C bond, but amorphous chromic oxide is an exception to this rule. Lazier and Vaughn<sup>230</sup> studied the conditions under which chromic oxide is prepared as a hydrogenating catalyst, and found that it is best obtained by heating a thin layer of ammonium dichromate. The reaction product obtained is not homogeneous, but consists of multicolored particles. It is assumed that the darker particles are catalytically active because, by heating in a thin layer, an inactive light-green oxide is obtained. By heating the active product above 500° and glowing, it is converted into a lighter-colored inactive oxide. Although the activity of chromic oxide catalyst for hydrogenation is practically destroyed by heating to 500°, its activity in the synthesis of methanol remains unchanged. In the catalytic decomposition of alcohol with an active catalyst, about 50 per cent is dehydrogenated and 50 per cent dehydrated; after heating the active catalyst up to 500°, the dehydrogenation is suppressed. An x-ray investigation of active chromic oxide catalyst for hydrogenation showed that it contains amorphous material which disintegrates on heating to 500°. A chromium catalyst prepared by heating chromium oxalate or chromium nitrate does not catalyze hydrogenation. The precipitates obtained from trivalent chromium salts or chromium solutions after reduction with alcohol and those obtained by precipitating with ammonia are differentiated by their color after drying, and by their texture. While the former are dark green in color and form glassy, gel-like masses, the latter are light green in color and powder-like in form. However, they do not differ in their catalytic activity. By precipitating with alkalis instead of ammonia, catalysts of lesser activity are obtained. The best catalyst has been found to be the one obtained by precipitation of a chromium nitrate solution

with ammonia. This catalyst yielded 86 per cent ethane in the hydrogenation of ethylene; 43 per cent propane in the hydrogenation of propylene, and 95 per cent octane with octylene; in the dehydrogenation of cyclohexane, a small amount of benzene was obtained.

Highly active chromium oxide gel, precipitated from a chromium nitrate solution by the addition of ammonia and drying, has been claimed as a catalyst in the hydrogenation and dehydrogenation of hydrocarbons. By the use of this catalyst, propane has been converted into propylene at about 400°; likewise, unsaturated hydrocarbons were converted into saturated hydrocarbons by passing them over this catalyst in the presence of hydrogen at 325–550°. <sup>274</sup>

A chromium catalyst suitable for the oxidation of carbon monoxide, as well as for the preparation of methanol and higher alcohols, has been proposed by DuPont. <sup>103</sup> A solution of a six-valent chromium compound was mixed with a soluble hydroxide and with the salt of a heavy metal, the hydroxide of which is oxidized by a chromium compound. For example, iron sulfate or manganese sulfate is treated with ammonia and the solution mixed with chromic acid. The precipitate is washed, dried, and pressed.

It has been claimed by Adadurov, Gernet and Chitun<sup>4</sup> that an oxidation of sulfur dioxide to sulfur trioxide to the extent of about 96–97 per cent is possible with the use of a contact mass, chromic oxide-stannic oxide at 450–460°. The origin of a zeolite structure was considered responsible for the greater increase in space conversion. The slight sensitiveness to poisoning of the chromic oxide catalyst activated by stannic oxide is remarkable when compared with that of the vanadium catalyst. Substituting other activators for tin gave no satisfactory results. Only aluminum oxide-chromic oxide at temperatures above 530° gave a yield of 90 per cent.

Assuming that sintering and recrystallization are responsible for the decrease in catalytic activity, Adadurov and Gernet<sup>3</sup> proposed, as a definite requirement for substances serving as activators for chromium catalysts, an increase in the thermal stability. To meet this condition, they suggested that the ion of the element serving as activator should be as large as possible in comparison with the ions surrounding it, and that it should possess, if possible, many valency gradations and have the lowest valency. They found that chromium-tin-antimony catalyst may be considered heat-resisting because a chromium-tin catalyst containing 3 per cent antimony chloride gave results as shown in Table 5.

Kutzelnigg and Wagner<sup>225</sup> investigated the influence of physical properties of the catalyst chromium oxide on its catalytic activity in the oxidation catalysis of potassium ferrocyanide solution by oxygen; they found that the preparation temperature of the chromium catalyst had a great influence on the catalytic activity. At 105°, dried chromium hydroxide is only slightly active; starting with 250°, the activity increases, attains its maximum at 450°, and then drops rapidly to zero; at 200°, a second maximum is attained, but the activity is considerably less than the first. An x-ray examination of chromium hydroxide shows that the



Table 5. (Adaduwow and Gernet.)

Catalyst	Hours of Heating	Temperature (°C.)	Space Velocity per hour	Yield (%)
Cr-Sn-Sb	—	400	60	99.0
	3	600	—	98.7
	7	410	—	98.5
	7	432	100	97.8
	7	452	140	96.8
	20	430	60	98.4
	20	448	140	96.7
	—	560	81	92.0

most active form is amorphous (green-brown) and the most inactive form is crystalline (green). All the preparations, including those glowed at 900°, were comparatively finely dispersed. In the series of preparations blackened by oxygen adsorption, a sharply defined maximum of the oxidizing action was attained at 300°.

The next in the series of catalytic activity is a very finely dispersed chromium oxide obtained by the decomposition of mercurous chromate at 600°. The comparatively coarsely dispersed green chromium oxide has the least activity.

The oxidizing action of catalyst preparations from ammonium chromate, chromium oxalate and chromium nitrate lies between the above limits and decreases according to this sequence without indicating definitely its dependence on the particle size.

Equimolar amounts of chromium oxide and magnesium oxide are mixed with an aqueous chromium oxide solution, evaporated to dryness, pulverized and reduced in a stream of hydrogen. This catalyst is suitable for destructive pressure hydrogenation.<sup>280</sup>

In the dehydrogenation of saturated hydrocarbons to olefins, a mixture of aluminum oxide and chromic oxide prepared by precipitating chromic oxide from a solution in the presence of powdered or granulated aluminum oxide at a temperature of 500–700° was used. The saturated hydrocarbons were converted directly into olefins such as ethylene, propylene or isobutylene. Dilution with inert gases or with an olefin which will combine with the liberated hydrogen has been recommended. This is true of ethylene in the dehydrogenation of higher hydrocarbons.<sup>45</sup>

Dehydrogenation of alcohols and hydrogenation of esters, aldehydes and ketones is successfully carried out with a catalyst comprising the oxides of cadmium and zinc partially combined with chromic oxide in the form of a chromite. In the preparation of this catalyst, 62 g. of cadmium nitrate were dissolved in 150 cc. of water and added to 574 g. of zinc sulfate dissolved in 2 liters of water. To this mixture is added 2.2 liters of a solution containing 305 g. of ammonium chromate neutralized with ammonium hydroxide. The precipitate obtained is washed, dried and heated in a muffle furnace to 400° for 4 hours, whereby the mixture is converted into a black powdery product with liberation of ammonia and nitrogen. A loss of 25 per cent in weight was recorded.<sup>106</sup>

Connor, Folker and Adkins<sup>86</sup> prepared a copper-chromium oxide catalyst for catalytic hydrogenation.

**Molybdenum.**—The investigation of Slotboom<sup>359</sup> on the preparation of molybdenum catalysts for catalytic hydrogenation indicates that the initial material from which a catalyst is prepared should not be a chemically pure basic substance. A catalyst prepared from ammonium molybdate or molybdenum disulfide (molybdenite) may be used successfully in the hydrogenation of naphthalene. Molybdenite is composed of 52.5 per cent molybdenum, 34.4 per cent sulfur, and about 10 per cent silicon dioxide with an admixture of iron, aluminum, magnesium, calcium, and others. The molybdenum disulfide is fused with sodium carbonate at 900°, washed with water, and the hot filtrate treated with 4*N* sulfuric acid, whereby a dark-green colloidal solution is formed, which may be impregnated on carriers. In the use of this catalyst, a yield of 81–87 per cent is effected, whereas the catalyst from ammonium molybdate shows a somewhat greater activity as indicated by a yield of 90–95 per cent.

It has been claimed that molybdic acid as a catalyst is especially active in pressure hydrogenation. This catalyst is prepared by dissolving molybdenum trioxide in ammonia, precipitating with hydrochloric acid in excess of 3 per cent, washing with water and heating for 2–10 hours at 415–450°, whereby the active crystalline form is obtained.<sup>361</sup>

Bahr and Petrick<sup>29</sup> studied various methods for the preparation of molybdenum trioxide catalyst, alone or on a carrier, and in a mixture with alkalis or metals, such as zinc, aluminum, or chromium. The molybdenum oxide prepared using zinc oxide was found to be the most active, and kieselguhr, the best carrier. A stable catalyst was said to be obtainable by mixing molybdenum trioxide, chromic oxide, and barium oxide in the ratio of 1 : 1 : 10, and was found suitable for the reduction of tarry phenols to cyclic hydrocarbons. It has been stated that molybdenum trioxide may become inactive as the result of poisoning due, not to sulfur or to the formation of higher-boiling compounds in the reaction products, but to the formation of the less active molybdenum dioxide.

The catalytic oxidation of toluene to benzaldehyde and benzoic acid in the vapor phase is usually carried out either with vanadium pentoxide or molybdenum trioxide, or a mixture of both. The preparation of this catalyst is based on a partial reduction of the higher oxides in an acid medium by metals, or mixing the reduced catalyst with the unreduced portion and layering on a carrier, such as ferro-chromium, which also serves as a reducing agent. For example, 10 parts of ammonium molybdate are dissolved in 15 parts of water, to which is added 15 parts of 10-per cent hydrochloric acid and 130 parts of ferro-chromium; the mixture is heated on a water bath, whereby the mass turns deep blue in color, evaporated to dryness, and the molybdenum oxide precipitated on ferro-chromium is glowed at 400–410°; blowing through air. The activity of this catalyst is most effective at 490–510°. In another example, it is recommended to dissolve 2.5 g. of ammonium molybdate in 25 parts of water, to which is added 12.5 parts of hydrochloric acid (sp. gr. 1.19) and 4.0 parts of zinc dust. The mixture is then heated to complete reduction, 5.0 parts of the obtained ammonium molybdate dissolved in 25 parts of water, and either ferro-chromium or pumice added. Further treatment of this catalyst pro-

ceeds as in the first example above. Tin may be substituted for zinc dust and is just as effective in its results.

When using a mixture of molybdenum and vanadium oxides, the procedure is as follows: to a solution of 7.0 parts ammonium molybdate and 0.85 parts ammonium vanadate dissolved in 15 parts of water are added 10 parts of 10-per cent hydrochloric acid and 150 parts of ferrochromium (particle size, 2-5 mm.); the mixture is stirred (color changes from purple to blue), evaporated to dryness on a water bath, and slightly glowed. The oxides are precipitated on the carrier and glowed in an iron tube at 400° by blowing through air. The iron tube (12 mm. in diameter) is plunged into a lead bath, the length of the catalyst layer (130 mm.), subjected to a stream of air and exposed to toluene vapors at 480-495°.<sup>54</sup>

Lolus, Polozow and Feofilow<sup>239</sup> patented a method for the preparation of a molybdenum catalyst for use in pressure hydrogenation of heavy hydrocarbons. Ammonium molybdate is heated in a stream of oxygen at 420-440° and then with a sodium sulfide solution to which solid sodium sulfide has been added; carbon dioxide is passed into this mixture until a precipitate is formed, acidified with sulfuric acid and diluted with water. The precipitate is washed with a solution of sulfuric acid-water, dried at 60° and, if desired, mixed with 5-20 per cent aluminum-iron or chromium oxide.

The I. G. Farbenindustrie A.-G.<sup>140</sup> patented a preparation for a pressed molybdenum catalyst from a mixture of molybdenum oxide, zinc oxide and magnesium oxide. This mixture is stirred with water to form a paste, dried at 120° and the solid substance broken into pieces and ground into a powder. To this material is added 10 per cent of the dry powder or of the original mixture, stirred together, water added, and the resulting mass pressed into a mold.

Galle and Michelitsch<sup>156</sup> state that molybdenum with respect to hydrogen sulfide and sulfur compounds shows a greater stability up to 600° under atmospheric pressure. Molybdic acid by increasing temperature shows an increase of sulfur from hydrogen sulfide. A precipitation of sulfur takes place at a temperature as low as 390°, the following reaction being assumed:  $\text{MoO}_3 + 2\text{H}_2\text{S} \longrightarrow \text{MoOS} + 2\text{H}_2\text{O} + \text{S}$ . The formed MoOS with respect to hydrogen sulfide shows great stability. Molybdenum sulfide with respect to hydrogen sulfide shows extreme stability even with high pressures and cannot be converted into a higher sulfide, whereas molybdenum alone under pressure adsorbs small amounts of sulfur from hydrogen sulfide. Concerning the behavior with respect to hydrogen, it is stated that molybdenum disulfide is very stable even at high temperatures and pressures. Molybdenum trisulfide separates one sulfur atom with formation of molybdenum disulfide. Molybdenum oxy-sulfide may be more readily reduced than the oxygen-free molybdenum compounds.

In hydrogenation of a sulfur-containing benzene without pressure, molybdenum trisulfide is gradually converted into molybdenum disulfide with precipitation of sulfur. Molybdenum disulfide prepared by reduction of molybdenum trisulfide using a mixture composed of 10 per cent by volume hydrogen sulfide and 90 per cent by volume hydrogen had a higher

desulfurizing ability than molybdenum disulfide obtained by reduction with pure hydrogen. It is used as a catalyst. In pressure hydrogenation of butyl mercaptan, molybdenum trisulfide was converted into a molybdenum oxide compound, splitting off sulfur, and then into molybdenum disulfide. In the hydrogenation of benzene contaminated with carbon disulfide, using molybdenum trisulfide as a catalyst, the latter is converted into molybdenum disulfide with liberation of elementary sulfur and hydrogen sulfide. Thereby molybdenum disulfide first acted as a hydrogenation catalyst of sulfur-containing compounds and then hydrogenated benzene.

**Tungsten.**—Several methods for the preparation of tungsten catalysts were patented by the I. G. Farbenindustrie A.-G.<sup>132, 133</sup> A catalyst giving excellent yields in the pressure hydrogenation of mineral oils is obtained when ammonium para-tungstate is heated with hydrogen sulfide at temperatures up to 410° under 5 atmospheres' pressure for 24–36 hours in the absence of air. The tungsten sulfide formed is molded under a pressure of 200 atmospheres and heated in a stream of hydrogen up to 430°.

In another case, hydrogen sulfide is passed into a solution of tungsten trioxide in aqueous ammonia until golden yellow crystals of ammonium tungstate are precipitated out; the mixture is evaporated to dryness, decomposed at 300° in a stream of hydrogen, and the resulting oxygen-free tungsten disulfide formed is pressed into molds. This catalyst also gives good results in pressure hydrogenation.

Ammonium tungstate, specially treated, is a very active and stable catalyst suitable for the hydrogenation and reduction of carbon-containing compounds at slowly increasing temperatures. For example, it may be obtained in a highly active state by passing nitrogen over ammonium tungstate at 400° to remove water and ammonia, then leading hydrogen containing 10 per cent meta-cresol through the mixture at the rate of 20 liters per hour, followed by the addition of hydrogen and hydrogen-meta-cresol at temperatures up to 850°.<sup>131</sup>

Tungsten disulfide, or a mixture of tungsten disulfide with zinc sulfide, magnesium sulfide, or aluminum sulfide, or a mixture of vanadium, chromium, molybdenum, manganese, rhenium, cobalt and nickel sulfides, may be used for the hydrogenation of tar, coal, and mineral oils. These catalysts are obtained by converting heavy metals into their sulfides and oxidizing.<sup>138</sup> Metal sulfides precipitated from sulfo- salts may be used to advantage in pressure hydrogenation of fuels. A freshly prepared solution of 1/2 mol titanium tetrachloride in benzene is treated with water and one mol ammonium sulfotungstate, with cooling. The precipitate is filtered, washed with low-boiling solvents, such as acetone or alcohol, and treated with hydrogen at 300–400°. The resulting gray-black mass is pressed into molds. Likewise, catalysts may be prepared from ammonium sulfotungstate and ferrous sulfate; nickel chloride and ammonium sulfovandate; ferric chloride and ammonium sulfostannate in alcohol, or an aqueous solution of one mol cobaltous chloride with a 5-per cent aqueous solution of ammonium sulfotungstate.<sup>141, 142</sup>

**Vanadium.**—In the preparation of vanadium catalyst, either vanadium pentoxide or the vanadate is used. For the oxidation of sulfur dioxide to sulfur trioxide, or for preparing anthraquinone from anthracene or benzaldehyde, benzoic acid from toluene, or phthalic acid from naphthalene, heating vanadium pentoxide to its melting point and using it as a catalyst, either in granular form or as a powder,<sup>329</sup> is recommended. Yefremow and Rosenberg<sup>414b</sup> proposed a method for precipitating vanadic acid on asbestos. The Gas Light and Coke Co.<sup>157</sup> suggested precipitating a vanadium catalyst on asbestos for the oxidation of toluene in the vapor phase. Fifteen grams of asbestos fibers are dipped into a hot solution containing 30 g. ammonium vanadate dissolved in a liter of water and 3 cc. aqueous ammonia (sp. gr. 0.9) to which are added slowly with constant stirring 107 g. ferrous sulfate dissolved in 450 cc. water and 60 cc. ammonia solution, drop by drop, to alkalize the mixture. After stirring for an hour, the precipitate is filtered and washed with water, the mixture molded into sticks, dried in an oven and crumbled, yielding 70 g. of the catalyst.

Another method for preparing a vanadium catalyst has been patented by the Barrett Co.<sup>40, 41</sup> To 21 parts ammonium metavanadate stirred to a paste with 15 parts of water on a water bath is added 34 parts oxalic acid; the mixture is heated until no more carbon dioxide is given off and then added to 8.5 parts of concentrated ammonia solution. This solution is mixed with the carrier and dried and the substance obtained heated in the presence of air or in an atmosphere of reducing gases.

The method of preparing vanadium catalyst for use in the manufacture of sulfuric acid by the contact process consists in treating calcium vanadate with a potassium carbonate solution and at the same time passing carbon dioxide into the mixture. After separation of the precipitates, the filtrate is treated first with a potassium silicate solution then with a barium chloride solution, the precipitate containing the vanadium filtered off, molded and dried. Calcium vanadate may also be dissolved in hydrochloric acid and the calcium precipitated from the solution as a hydrate by the addition of potassium hydroxide. Water glass is added to the filtrate and the mixture treated as above.<sup>322</sup>

Another catalyst used in the contact process of sulfuric acid manufacture is a silicon oxide-vanadium ore containing 10–25 per cent of vanadium pentoxide. This material is pre-treated with hydrochloric acid, followed by treatment with an equal amount of sulfuric acid until no visible conversion with sulfuric acid (taken in amount not less than that of hydrochloric acid) takes place; sodium and potassium sulfate are added in amounts equivalent to that of vanadium pentoxide, and the mixture heated until sulfur trioxide fumes are given off. The resulting product is roasted in an atmosphere of sulfur oxides.<sup>159</sup>

In sulfuric acid catalysis, the behavior of vanadium catalysts varies, depending on the physical conditions under which they are prepared, as well as the nature of the vanadium compound used.<sup>1</sup> In comparing the catalytic activity of various metavanadates, such as sodium, potassium, tellurium, and silver, in the oxidation of sulfur dioxide, Cannori and de Pava<sup>72</sup> ascertained that the greatest catalytic activity was shown by the

salts of sodium and silver and the least by tellurium; the activity of potassium lies between these two extremes. The activity changes thereby in the same sense as the activity of the corresponding acid vanadates in spontaneous reduction; this is recognized by loss of oxygen in solidification.

The behavior of sodium polyvanadate,  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$ , is similar to that of vanadium pentoxide, investigated by Neumann.<sup>256a</sup> However, it shows a slightly greater activity in the temperature range  $475\text{--}550^\circ$  but does not attain the value of the metavanadate. From this it may be concluded that the catalytic action is a function of the state in which vanadium pentoxide is held together. In comparing the catalytic activity of  $3\text{SnO}_2 \cdot \text{V}_2\text{O}_5$ ,  $\text{Na}_2\text{O}$  and  $2\text{Na}_2\text{O} \cdot 3\text{MoO}_3 \cdot \text{V}_2\text{O}_5$  with sodium vanadate, it has been found that the second is more active than sodium vanadate; as a matter of fact, it produces the highest yield of sulfur trioxide (98.4%) at  $440^\circ$ , indicating that molybdenum is an active activator for vanadium catalysts. The sodium-molybdenum-vanadium catalyst is apparently suitable for industrial application.

Phthalic anhydride is formed when phthalic acid is heated. It can be made on a large scale by passing the vapor of naphthalene and air over the oxide of vanadium at about  $500^\circ$ , using aluminum as a carrier. In order to change the structure of the carrier, heating it has been suggested. Therefore, the original components of the catalyst are mixed together, subjected to 3,000 atmospheres' pressure to form tablets, and heated for several hours at  $600^\circ$ .<sup>301</sup>

**Titanium.**—Rudisill and Engelder<sup>304</sup> studied the catalytic activity of titanium as a function of the method used in the preparation of the catalyst and found that the titanous hydroxide precipitated from titanium oxy-sulfate by the addition of ammonia or prepared by the hydrolysis of diluted solutions of titanous chloride is the most active and stable catalyst, particularly when the sulfate radical or the chloride ions are removed by washing, in the catalytic decomposition of alcohol at  $350^\circ$ , which gives the highest yield of ethylene. When titanium catalyst is precipitated from a titanium oxalate solution, its activity is least, giving mostly ethane. It was found that grinding titanous hydroxide or titanous oxide (titanium dioxide) catalyst increased its activity, and that a higher yield of ethylene and ethane was obtained. An increase in the glowing temperature of titanous oxide above  $350^\circ$  decreased the velocity of alcohol decomposition, especially the velocity of dehydrogenation.

The I. G. Farbenindustrie A.-G.<sup>134</sup> proposed oxidizing metallic chlorides in a gaseous phase as a method for preparing finely dispersed oxides, particularly titanous oxide. For example, titanium chloride is oxidized in purified carbon monoxide under regulated operating conditions, whereby titanous oxide of varying degrees of dispersion may be obtained.

A titanium catalyst may be prepared from one-half mol of freshly precipitated titanous chloride in benzene to which is gradually added one mol of ammonium sulfotungstate in cyclohexylamine followed by cooling in water. The precipitate formed is separated by filtration using suction, and treated with dry hydrogen and hydrogen sulfide at  $300\text{--}400^\circ$ . A

gray-black mass is obtained which is molded into tablet form and used as a catalyst in hydrogenation.<sup>206</sup>

**Thorium.**—Thorium oxide preparations show varied behavior in catalytic processes. Thorium oxide may be obtained from thorium hydrate dried at 340°. Thorium hydrate is precipitated from thorium sulfate by the addition of ammonia. The substances obtained by heating at low temperatures contained salts of ammonia (up to 2.4%). Thorium meta-oxide may be obtained either from thorium oxalate or thorium nitrate by heating to 750°. The catalytic action of these preparations was determined in the dehydration of alcohols at 340° in a stream of carbon dioxide. The normal thorium oxide and the meta-oxide are crystalline in structure and identical in action. The thorium oxide obtained according to ordinary methods of preparation is amorphous, stable at temperatures above 300°, and active. It is apparent that the structure of thorium oxide has no influence on its dehydrogenation action, the crystalline and amorphous form being equally effective.<sup>235</sup>

A thorium oxide gel having a high adsorption power as well as a good catalytic action may be prepared by peptizing freshly precipitated thorium hydroxide with acid-acting substances and continuous stirring. The highly concentrated hydrosol obtained is dehydrated under mild conditions and heated slowly to 500–600°. <sup>125</sup> It has been found that cerium oxide greatly influences the catalytic properties of thorium oxide.

The catalytic action of thorium oxide-cerium oxide mixtures depends on their method of preparation, washing, drying and glowing. In the first place, the optimum effect of the oxide mixture corresponds to a definite ratio of the components in the mixture<sup>206a</sup> which is 99 : 1, and may be observed only in mixtures precipitated as carbonates, but not as oxalates, or prepared by heating the nitrates; better results may be obtained by glowing at 550° than at 720°, the latter temperature corresponding to minimum activity.<sup>136, 137</sup>

Iwannikow<sup>209b</sup> studied the preparation of ethyl acetate from alcohol vapor led over catalyst copper acetate + 0.5–50 per cent thorium acetate or nitrate at 180–350°. The catalyst was prepared as follows: thorium acetate or nitrate is dissolved in 5–8 per cent copper acetate solution, the mixture heated to 50–90°, and treated with an excess of concentrated sodium hydroxide solution. The precipitate separated is filtered off, washed with hot water, and dried at 120–180°.

Metals, such as cerium, thorium, bismuth, uranium, aluminum, cadmium, and iron are insoluble in water, but form phosphates soluble in phosphoric acid. Thorium oxide or thorium hydroxide, or any other salt soluble in concentrated phosphoric acid, is dissolved in an excess of 89–100 per cent phosphoric acid (the amount used being about double or even tenfold), the mixture poured into water, and the precipitated phosphates filtered by suction and washed. The phosphates may be activated by the addition of antimony, chromium, cobalt, copper, magnesium, manganese, nickel, silver, tungsten, zinc, or tin (the phosphates of which are insoluble in concentrated phosphoric acid), or their oxides or phosphates. A catalyst so prepared is suitable for the formation of formalde-

hyde by the oxidation of methane by air; acetaldehyde from acetylene and water vapor; formaldehyde and acetaldehyde from ethylene and oxygen, and alcohol from ethylene and water. The preparation of a uranium oxide catalyst is based on the same principle. Two parts of uranium oxide mixed with one part bismuth chloride are dissolved in 10 parts of 89-per cent phosphoric acid at 160°. After cooling, the liquid is poured into 75 parts of water, the precipitate decanted, filtered by suction, washed, and dried at 120°. The contact mass is characterized as a highly active, porous catalyst, stable at high temperatures.<sup>89</sup>

**Aluminum.**—In the preparation of alumina for use in catalysis by precipitation and drying, heating not above 400° and testing for solubility in acids and alkalies are suggested. To possess good catalytic action, alumina must dissolve readily in warm hydrochloric or sulfuric acid, as well as in concentrated sodium hydroxide solution. Alumina is used for the dehydration of aliphatic, as well as cyclic, alcohols.<sup>208</sup> Unglowed aluminum catalyst prepared from aluminum hydroxide strongly effects the condensation action on acetone at 455°. <sup>6</sup>

In preparing alumina as a dehydrogenation catalyst, it has been stated by Alexejewsky and Prejis<sup>14</sup> that the best catalysts are obtained by precipitation of aluminum hydroxide from sodium aluminate with hydrochloric acid or from aluminum sulfate with ammonia. In the catalytic decomposition of alcohol with a catalyst prepared from aluminum sulfate, the formation of large amounts of mercaptans was observed.

A mixture of aluminum, cerium and cadmium nitrates precipitated with an alkali phosphate to which an alkali is added slightly in excess has been found to be a suitable catalyst in the oxidation of hydrocarbons. The catalyst is treated before or during use with a corroding gas, such as hydrogen chloride or nitrosyl chloride.<sup>126</sup>

A catalyst for converting acetic acid in the presence of water vapor into acetone is made up of a mixture containing aluminum oxide. The catalyst preparation involves the reaction of an aluminum amalgam or an aluminum alloy with a calcium nitrate solution, whereby finely dispersed aluminum oxyhydrate is formed as a film which dehydrates when inert gases or vapors are passed over it.<sup>242</sup>

An aluminum oxide catalyst may also be prepared by precipitation with ammonium hydroxide from aqueous aluminum containing pumice in suspension (0.1 per cent by weight of aluminum), washing the aluminum oxide precipitate deposited on powdered pumice, and drying at 30–40°. <sup>253</sup>

The use of a mixture of equimolecular amounts of aluminum chloride and phenol has been suggested as a substitute for aluminum chloride in the hydrogenation of hydrocarbon oils.<sup>174, 175</sup>

**Zinc.**—An active catalyst in the synthesis of methanol from carbon monoxide and hydrogen at increased temperatures and under 150 atmospheres' pressure with a yield of 200–250 g. methanol per cc. catalyst space per hour is prepared as follows: anhydrous cupric oxide is intimately mixed with large amounts of zinc oxide in the ratio of 4 parts copper to 96 parts zinc oxide. A solution of zinc and copper salts, such as the nitrates, or their salts with organic acids, is treated with a boiling solution



of an alkali, the precipitate filtered, dried, and reduced at ordinary pressure with hydrogen or carbon monoxide at the lowest temperature possible in order to decrease local overheating.<sup>352</sup> A methanol catalyst may be obtained from zinc carbonate or zinc bicarbonate, using chromic acid.<sup>197</sup> Zinc oxide catalyst for catalyzing organic reactions may be prepared by adding to an ammonium nitrate solution a mixture of zinc oxide and chromic oxide and heating the mass.<sup>81</sup>

For the preparation of methanol and other oxygen-containing organic compounds of carbon monoxide and hydrogen, it was suggested using zinc-containing chromium in the ratio of 9 parts zinc and one part chromium as a catalyst. A mixture of zinc carbonate or basic zinc carbonate and a chromium compound, such as zinc chromate or basic zinc chromate, is heated in the presence of hydrogen. It is prepared by reacting a soluble chromium salt with zinc carbonate or basic zinc carbonate, or by reacting a soluble zinc salt with a chromate or bichromate in the presence of a soluble carbonate, or by treating freshly precipitated zinc carbonate or basic zinc carbonate with chromic acid in an aqueous solution.<sup>370</sup>

For the conversion of mineral oil, tar, and coal, the use of a catalyst obtained by the reduction of zinc oxide and molybdic acid at 480°<sup>124</sup> has been suggested. A chromium zinc catalyst consisting of three molecules of zinc oxide, one molecule of chromic oxide, and twenty molecules of water is mixed for one hour in a mill, 0.5 per cent cupric oxide in the form of cupric nitrate is added, and the mixture is dried and reduced in a stream of hydrogen at 300°.<sup>257</sup>

Organic compounds from carbon monoxide and hydrogen may be synthesized over colloidal catalysts, converted into a gelatinous mass, washed by decantation, and molded into form after removal of excess water; drying of the catalyst should take place at a low temperature. A zinc catalyst prepared according to this method is obtained when a 20-per cent zinc nitrate solution is added to a sodium carbonate solution and the alkali content maintained at 50 per cent in excess. The precipitate is decanted at room temperature, washed, dried at room temperature, ground and molded.<sup>66</sup>

In the study of the synthesis of aliphatic alcohols by catalytic reduction of carbon monoxide over zinc oxide, Natta and Rigamonti<sup>254</sup> ascertained that the increase in the alkali content of the catalyst caused a displacement in the ratio of methanol to higher alcohols in favor of the latter; a considerable amount of isobutyl and *n*-propyl alcohol accompanies the formation of methanol. The zinc catalyst for use in the synthesis of methanol is prepared by precipitating it as a colloidal oxide, hydroxide, or carbonate, removing most of the solvent by decanting off the liquor at ordinary or even lower temperature, and molding the precipitate by hot compressing. The catalyst obtained is dried at ordinary or even lower temperature, and no attempt is made to separate any or all components other than zinc from the material obtained.<sup>99</sup>

Kostelitz and Hüttig<sup>221</sup> investigated the influence of conditions under which a catalyst such as zinc oxide is prepared with respect to its activity in the decomposition of methanol. Basic zinc carbonate pressed into

tablet form under 50–5000 atmospheres' pressure was converted into zinc oxide at 300° in a stream of methanol or ethanol vapor and the catalytic behavior of the catalyst so prepared was observed with respect to these two alcohols. The catalytic activity of the zinc oxide catalyst prepared in a stream of methanol vapor was found to be greater than that exposed to air (Weichensteller effect). The catalytic activity relating to the volume unit increases with an increase in compression pressure, while the catalytic activity relating to the weight unit of zinc oxide decreases with an increase in compression pressure.

A considerable loss of catalytic or adsorptive power has been proved at temperatures far below those at which visible sintering of the surface takes place.<sup>228, 383a</sup> The preservation of a heterogeneous active surface is assisted by depositing the catalyst on some refractory support, acting by fixing the atoms more firmly, so that they are less likely to move under moderate thermal agitation.<sup>22</sup>

According to Constable the essential feature for the production of catalytically active copper is the sudden liberation of free copper atoms under conditions in which the kinetic energy of the atoms is insufficient to cause collapse of the active structure. Chemical changes may be active enough to cause rearrangements of the surface structure. In some of these the catalytic activity increases with use, up to a maximum, because new active centers are formed by movement of the atoms. Any change in the surface arrangement which tends to greater regularity diminishes catalytic power as a rule; a disintegrating action increases the catalytic power, both by increasing the total extent of the surface, and by increasing the number of active patches.

Catalysts for the synthesis of alcohols may also be prepared by treating zinc or its alloys with nitric or hydrochloric acid containing copper, chromium, cobalt, or manganese, or salts of these elements, whereby the surface of zinc or its alloys is etched and covered with fine particles of a metal.<sup>393</sup> Another patent<sup>394</sup> by the same patentee gives a method for preparing catalysts for gas reactions. Oxides or carbonates of zinc, copper, or iron in either powder, granular, or platelet form are heated at 100–105° with a definite amount of chromic acid or a salt of chromium (chromate) poured over the mixture.

**Copper.**—Kostelitz and Hüttig<sup>221a</sup>, in their study of catalytic decomposition over mixed catalysts CuO–ZnO, found that the dependence of their activity on temperature may be expressed by the following equation:  $\ln K = \alpha/T + \beta$ , where  $\alpha$  and  $\beta$  are constants and have molecular kinetic significance. It has been stated that metals and their alloys of low catalytic activity may be converted into catalysts of high activity by increasing their surface with alternate treatment of chlorine and ammonia.<sup>349</sup> The preparation of aldehydes from alcohols may be effectively carried out by using a copper catalyst. A copper tube is filled with copper wire, copper or nickel nitrate solution added, the hydroxide precipitated with ammonia, heated up to 300°, and reduced at this temperature with hydrogen.<sup>398</sup>

For the oxidation of ammonia, methanol, or methane, or the combustion of carbon monoxide by the action of water in the presence of hydrogen,

is recommended a catalyst obtained by heating silver or copper cyanamide or their mixture in the presence of air, the cyanamides being obtained by the precipitation of a cyanamide solution with silver nitrate or cupric chloride. The catalyst is activated by adding vanadium-molybdenum-ferro or ferric cyanide to the cyanamide.<sup>258</sup>

Melted cupric oxide which has been pulverized and reduced, partially or completely, in a stream of hydrogen, may be used in the dehydrogenation of alcohols, such as butyl alcohol.<sup>234</sup> A method for producing an active copper catalyst is described by Lance.<sup>226</sup> A copper foil rolled on a corrugated surface is plunged into an aqueous solution of ammonia, exposed to air, placed in distilled water, and heated until the green coating turns brown. After drying, the precipitate is reduced by hydrogen on heating. A catalyst which has a large surface and is a good heat conductor is said to be produced by this method.

A copper catalyst may be obtained from copper formate, acetate, oxalate, malonate, or succinate as stated by Constable.<sup>88</sup> A catalyst successfully used in general catalytic reactions has been prepared from porous metals or their alloys by treating with chemical reagents which dissolve one component but leave the others intact. For example, brass treated with alkali and then with dilute acid; alloys of copper and calcium with dilute acid; alloys of tin and sodium with water or alkali. Similarly, active porous metal alloys of lead-tin, copper-manganese, and others.<sup>122</sup>

In the case of a copper catalyst prepared from the precipitated hydroxide, it has been shown that the activity is a function of the precipitation temperature. The high-pressure synthesis of methanol indicated varying activity of copper catalysts prepared from precipitated cupric salt with ammonia at different temperatures (0°, 10°, 22°, 55°, 85° and 100°), dried at 110° and 220° respectively in a stream of nitrogen to eliminate the salts of ammonia. The greatest activity was obtained when the catalyst was precipitated at high temperatures. This catalyst causes not only the decomposition of formaldehyde, but also the formation of methyl formate; the greater the catalytic activity of the catalyst, the greater the amount of methyl formate produced. The dried gels of the catalyst contained very small particles, and the smaller the particles the greater the activity. On the other hand, the size of particles is a function of the precipitation temperature. Therefore, the lower the precipitation temperature, the smaller the size of particles. By drying, the size of particles is increased; those which contain much water, or are the result of low-temperature precipitation, attain greater size than those containing less water and obtained at higher precipitation temperature. Thus two diametrically opposed influences are involved, and this fact is considered as an explanation for the decrease in particle size.<sup>156</sup>

Catalytic substances containing stabilized hydrated cupric oxide are prepared by precipitation of cupric hydroxide from a copper salt solution, and heating the precipitate in the mother liquor until the desired dehydration is effected. As stabilizing agent is added an alkali metal salt, such as sodium sulfate or sugar.<sup>246</sup>

Copper alloys consisting of one or more metals possessing the ability

to oxidize in the presence of air on heating and particularly of metals which, under similar conditions, oxidize more readily in an oxidizing atmosphere and when used in the metallic state may be readily reduced, are considered as catalytic substances. For example: (1) copper, 85 per cent, magnesium, 15 per cent; (2) copper, 75 per cent, iron, 10 per cent, magnesium, 15 per cent; (3) copper, 50 per cent, zinc, 10 per cent, calcium, 40 per cent; (4) copper, 40 per cent, nickel, 40 per cent, magnesium, 20 per cent, and others.<sup>192</sup>

Partial oxidation of organic compounds in the vapor phase, such as oxidation of low molecular monovalent alcohols into aldehydes, ketones and acids, of ethylene to formaldehyde, or of toluene to benzaldehyde and benzoic acid, is advantageously carried out with catalysts containing 95.0–99.75 per cent of cupric oxide or silver oxide and 0.25–5.0 per cent of an oxide of a rare earth. The silver or copper nitrate is precipitated in a dilute nitric acid solution together with a solution of a nitrate of a rare earth. For example, samarium on pumice carrier is heated in a stream of oxygen or air to 450–600° whereby the copper nitrate and the nitrate of the rare earth are converted into their oxides.<sup>91</sup>

A catalyst consisting of reduced copper and calcium oxide with a copper content not exceeding 50 per cent is another catalyst which may be used in the synthesis of methanol at 150–450° under a pressure up to 300 atmospheres. This catalyst is prepared by dissolving 236 parts of calcium nitrate  $[\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$  and 100 parts of copper nitrate  $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$  in 1500 parts of water, precipitating the hydroxides by stirring into the mixture 120 parts of sodium hydroxide in 500 parts of water, pressing dry the precipitate, separating the nitrates, and washing and drying at about 150–200°. The substance obtained was reduced at a temperature not exceeding 350°; a temperature of 150–200° is preferable.<sup>298</sup>

Lead-copper and tin-copper catalysts are prepared by reduction of intimate mixtures of catalytically active compounds of low melting points with compounds of high melting points.<sup>139</sup>

Barker<sup>36, 37, 38</sup> in his patents presents a number of methods for preparing copper alloys. Alloys, especially those of iron and copper, manganese and copper, or manganese, lead and copper are surface-treated with acids, such as hydrochloric or nitric, in order to form a porous layer of the metal salt which is converted by calcination into the oxide. Alloys composed of 25 per cent manganese, 10 per cent lead and 65 per cent copper are oxidized superficially and then subjected to the action of reducing agents, whereby a porous metal surface is formed. In the preparation of iron-copper alloys for use in the oxidation of carbon monoxide to carbon dioxide or sulfur dioxide to sulfur trioxide, it is suggested substituting the hydrogen chloride used in the treatment for oxygen.

Solotow and Shapiro,<sup>388</sup> investigating the decomposition of methanol over copper-zinc catalyst, believed that the selective activity of the catalyst was dependent on the structure. At 220° the cupric oxide-zinc oxide mixture is reduced by methanol vapor, the cupric oxide reduced to the metal, forming a solid solution with zinc, and a partial reduction of zinc oxide with the formation of alpha brass. The higher the zinc

oxide content of the initial mixture, the greater the amount of zinc in the solid solution, increasing with increase in time of the catalyst's exposure. The rate with which zinc dissolves in alpha brass decreases with an increase in the zinc content.

A copper catalyst suitable in the catalytic reaction of  $\text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2$  was obtained by treating a copper sulfate solution with sodium carbonate, dissolving the precipitate with chromium trioxide in nitric acid, and precipitating the copper catalyst by ammonia.<sup>105</sup>

In surface combustion processes, in the removal of carbon monoxide from the exhaust gases of combustion engines, and for the oxidation of sulfur dioxide to sulfur trioxide, the mixture to be catalyzed is led continuously over a copper-chromium catalyst [ $\text{CuO} \cdot \text{Cr}_2\text{O}_3$  or  $\text{Cu}(\text{CrO}_2)_2$ ] at 500–600°, prepared by converting cupric hydroxide with a chromium trioxide solution forming  $\text{Cu}(\text{CrO}_4)_2$ , and heating. The cupric hydroxide is obtained by precipitating cupric nitrate with ammonia.<sup>103</sup>

The conversion of monohydroxy-aliphatic alcohols into their corresponding esters, such as ethyl alcohol into ethyl acetate (60 per cent), propyl alcohol into propyl propionate (55 per cent), and butyl alcohol into butyl butyrate (70 per cent) at 180–350°, is brought about by the use of a copper catalyst prepared from a copper acetate solution by precipitation with an alkali at 50–95° followed by the addition of 0.5–7.0 per cent uranium acetate to the filtered precipitate. It is then treated with concentrated sodium hydroxide solution, the black precipitate washed first with cold water then with water heated to 70–80°, then dried at 120–200°, powdered and heated in a stream of hydrogen at 200–300°.<sup>210</sup>

Schwab and Nakamura<sup>326a</sup> attempted to draw a relationship between the catalytic properties of magnesium oxide and cupric oxide catalysts in the decomposition of  $\text{N}_2\text{O}$  and the method of preparation used for these catalysts. The activation heats and action constants calculated by means of the Arrhenius equation are related to the known heat content and lattice structure of the catalyst. The findings indicate that in the case of magnesium oxide prepared from the hydroxide the activation heat by a simultaneous increase of the action constants increases with raised pre-treating temperature. With regard to cupric oxide, the activation heat with simultaneous strong decrease in the action constant decreases when the preparation temperature is raised. These results were interpreted in the sense that in the case of magnesium oxide the increase in the activation heat is caused by shrinking of the lattice extension and with it a decrease in the energy content, while in the case of cupric oxide the higher activation heat of the low-temperature preparations is related to the impregnation of the crystal surfaces in the amorphous material and to the higher action constant due to a greater adsorption capacity for  $\text{N}_2\text{O}$ .

Anissimow, Kraschennikowa and Platonow<sup>19a</sup> state that rhenium was found to have comparatively little activity as a catalyst in hydrogenation reactions, but that, when precipitated upon a ceramic carrier, it appears to be very active for the dehydrogenation of alcohol to aldehyde. However, it is less active than metallic copper. At 350°, a mixed catalyst composed of copper and rhenium was found to be more active than simi-

larly prepared copper catalyst alone. Therefore the addition of rhenium increases the catalytic activity of copper. On the contrary, at 450°, the activity of the copper catalyst is greater than that of the mixed copper-rhenium catalyst. The regeneration of rhenium catalyst in a closed vessel is effected by the oxidation of rhenium in oxygen at temperatures greater than 200°. In general, in catalytic oxidation reactions (ammonia, methane, and benzene) at high temperature, rhenium readily gives off volatile oxides. Therefore, in these cases, the use of perrhenate or rhenium alloy instead of rhenium is recommended.

#### ACTIVATION AND REACTIVATION OF CATALYSTS

The activation of a catalyst concerns itself with a specific treatment of the prepared catalyst in order to render it more efficient and more stable in performing its function in a catalytic process. The reactivation of a catalyst involves the measures to be taken in order to re-establish the catalytic properties of a spent catalyst. A catalyst may lose all or a part of its activity due to internal or external poisoning, or the loss in activity may be attributed to its own instability. While activation tends to improve the activity of a catalyst and to increase its life span before use in a catalytic reaction, reactivation regenerates a catalyst which has lost its catalyzing property during use in a catalytic reaction. Re-establishing the activity of a spent catalyst is an economical procedure. The problems involved in both the activation and reactivation of a catalyst are factors that must be considered in its selection for a particular process. Although each of these problems may have its individual solution in every catalytic process, they are to a certain extent related. Activation methods should not be overlooked in the technic of preparing catalysts. On the other hand, in choosing a catalyst for a particular catalytic process one should also bear in mind the possibilities for reactivating that catalyst once it has been used.

**Activation.**—If it were possible to know the factors involved and the conditions under which a catalyst is rendered active, the choice of a method not only by which it can be prepared, but by which it may be activated or its activity improved, would be facilitated. The induction of a catalytic reaction, however, has been the focus of interest. If molecules of high energy content and thermally activated are alone involved in a catalytic reaction, why is it that hydrogen and oxygen, for instance, react more readily if a trace of moisture is present? Semenov has shown that an exceedingly small number of active centers are necessary to set in motion a chain reaction which may culminate in an explosion. Semenov assumed for his purpose of calculation that these centers were thermally activated, and that a very small number of such centers required:

$$N_0 = \frac{Ae^{-E/RT}}{\tau}$$

where  $\tau$  is the life of the active center and the numerator represents Arrhenius' formula. Semenov doubts whether thermal activation is sufficient. It has been pointed out that water is essential for some chain

reactions, the union of sodium and chlorine, for instance. Wood<sup>413</sup> found that water assisted an atom of mercury to assume a metastable state. In all probability the primary reacting molecules, although possessing high translation energy, undergo certain internal disturbances.

Mendeleef<sup>246a, 246b</sup> foreshadowed in qualitative terms the recent developments of the quantum theory of activation of adsorbed molecules. All molecules are in a state of motion or oscillation. By contact with the surface of a solid the motions of the molecules are altered. A strain set up thereby may frequently alter the equilibrium of molecules and induce reactions which otherwise would not occur with an appreciable speed. In modern terms it means that the distortion of the adsorbed molecule

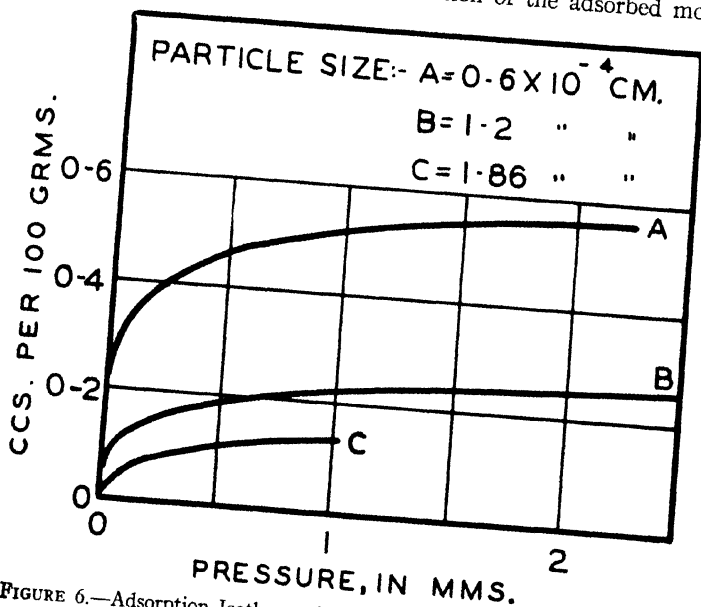


FIGURE 6.—Adsorption Isotherms for Hydrogen on Tungsten Powder at 180° (Frankenburger and Hodler<sup>181a</sup>).

brings about a reactive or excited state, which depends on the configuration set up during the vibration.

In considering activation for chemical reactions, the vibrational energy has recently received much attention in connection with the "transition state." Evans and Polanyi,<sup>118a</sup> treating the theory of transition states, pointed out that the distances between atoms in each molecule vary periodically as the molecules vibrate, and that the atoms consequently pass through states of differing potential energy. The different states have different reactivities determined by geometrical considerations.

The knowledge of the conditions under which a catalyst is highly activated is just as important as that of the conditions of reactivity of the reacting components in a catalytic reaction. The active places present in a catalyst indicate, energetically as well as structurally, properties dif-

ferentiating a crystal surface from an isolated atom. The total catalytic activity of a metal surface depends on: (a) the magnitude and character of the reachable surface; (b) the configuration of the metal atoms in the surface, and (c) the chemical nature and properties of the metal.

With respect to the size and character of the reachable surface, the activation of metal surfaces may be carried out in the first place by oxidation and reduction processes, as well as by mechanical and chemical pretreatment.

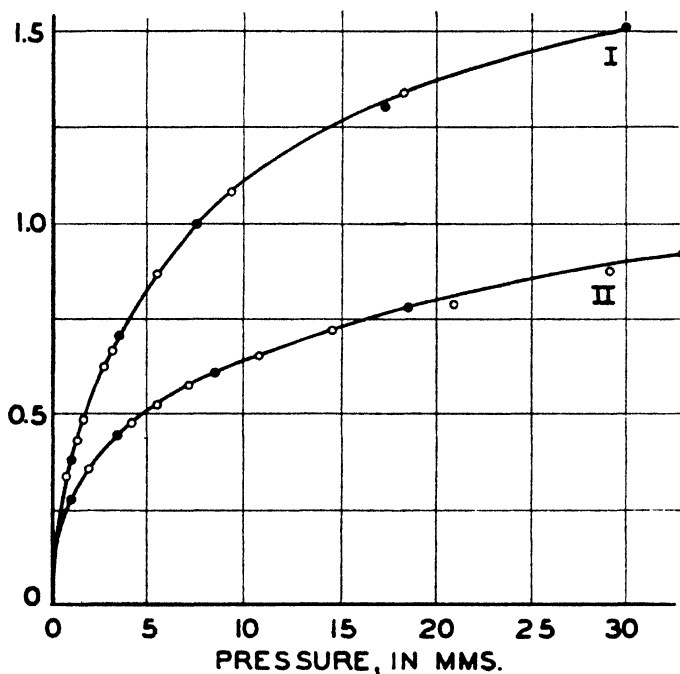


FIGURE 7.

It is recognized that the particle size of metal powders depends both on the temperature of reduction and on the fineness of the oxide from which it was prepared. The lower the temperature of reduction, the smaller the particle and the larger the surface for a given mass. When the temperature is raised the particles grow and sinter together, the surface area decreasing. In Figure 6 are shown the adsorption isotherms for hydrogen on tungsten powders of different particle size: (1)  $0.6 \times 10^{-4}$  cm.; (2)  $1.2 \times 10^{-4}$  cm.; (3)  $1.86 \times 10^{-4}$  cm. The adsorption varies with the surface area, but not in a perfectly linear manner.

Ward<sup>403a</sup> obtained adsorption isotherms for hydrogen on copper reduced at 150°C. (Figure 7, Curve I) and on copper after further sintering at 200°C. (Curve II). This shows a reduction of about 30 per cent in adsorptive power. Most active adsorbents are obtained by repeated alternate oxidation and reduction. Taylor and Burns<sup>378a</sup> state that the adsorptive



power of nickel reduced at 600°C. was only about 20 per cent of that found after reduction at 200°C.

Kingman<sup>216</sup> studied the degree of adsorption of hydrogen in various stages of reduction in a freshly prepared catalyst reduced by repeated treatment with hydrogen. The curves obtained indicate that, by measuring the extent to which reduction of the catalyst proceeds, a relationship to the amount of hydrogen adsorbed is found. The amount of hydrogen adsorbed first decreases, increasing after a minimum adsorption has been attained. This adsorption decrease has been attributed to a decrease in the reduced surface of the catalyst, the increase following being caused by the substitution of new active centers for old active centers which are enabled to adsorb without further reduction. Kingman postulates three possible types of adsorption in the adsorption of hydrogen on zinc and chromium oxides: (1) van der Waals' adsorption predominating at 80°; (2) adsorption accompanied by an activation with adsorption heat (20–30 cal.) which does not cause reduction of the catalyst and occurs at higher temperatures, and (3) irreversible adsorption—adsorption which disappears as soon as the catalyst is reduced and re-appears to a considerable extent only at 100°. It has been emphasized also that in the cold the gas adsorption may be just a loose accumulation at the metal surface which is readily reversed by an increase in temperature and a decrease in pressure. At higher temperatures the adsorption accumulation may be converted into a more permeable, irreversible character, not readily influenced by temperature and pressure changes. The presence of oxygen or hydrogen may cause surface activation of the metal. The gas present may be in an atomic state, *in statu nascendi*, in a metastable form, as a proton, an electron, or an ion. The relative ratio of these single factors depends on the conditions existing (Paneth). Apparently the forces of affinity present in diatomic gas molecules which are responsible for the neutral combination by chains are split up; therefore a part of the gas adsorbed in the metal surface is present in an active atomic form, which activates it. Activation by reduction may be carried out by passing the metal salts precipitated on a carrier through a zone of heated hydrogen and a concentrated gas zone. The zones are arranged so that one is below the other or so that the catalyst passes through the zones in directions opposite to each other. The tube forming the zones may be provided with powder sprayers, heat and cooling arrangements.<sup>332</sup>

Metal catalysts were found to be highly activated simultaneously with the formation of a large surface by treatment with mercury. These catalysts were prepared by mixing metals with mercury and distilling off the latter in high vacuum with elimination of gases reacting with the metals; a powder-like substance with a greater surface appears as the final product.

Centnerszwer<sup>76</sup> interpreted the activation of an aluminum surface as the dissolution of a "passive" surface layer. Aluminum in sulfuric acid is so strongly passive that it cannot be activated, not even by platinum. The addition of small amounts of chloride ions or bromide ions is sufficient to induce gradual activation. Centnerszwer was of the opinion that those

metals which decrease the overvoltage of hydrogen accelerate, in contact with aluminum, its dissolution in hydrochloric acid. The action of mercury is fundamentally different from that of other metals. Aluminum amalgam dissolved in 1*N* hydrochloric acid with a velocity 25 times greater than any other form of aluminum. This investigator sees in mercury a catalyst for the establishment of an internal equilibrium.

According to Pietsch and Josephy,<sup>276</sup> the catalytic effect of metals by recombining of hydrogen atoms and the hydrogen overvoltage of the same metals is inversely proportional. Thus palladium, in the series palladium, silver, copper, and lead, having a zero overvoltage, shows the greatest catalytic effect.

Silica Gel Corporation's (Reyerson)<sup>334</sup> activation method involves treating the metal with a salt solution of a metal standing lower in the voltage series until an ion exchange takes place. For example, a dehydrated silica gel is freed from gas in vacuum at 0°, saturated with hydrogen, treated with a nickel nitrate solution, and the precipitate reduced. The gel containing the reduced nickel is activated by treating it with a silver nitrate solution so that an ion exchange between nickel and silver takes place.

It has been pointed out by Quartaroli<sup>283</sup> that the activity of catalysts varies, the addition of some oxides hastening the decrease in activity, while other oxides stabilize catalytic activity. Sometimes an increase in the activity of a catalyst may be brought about by mechanical means, such as polishing, scraping, and etching the catalyst at points of contact with reaction gases; sometimes by electrochemical treatments, such as anodic oxidation, or by simply plunging the catalyst into a neutral or an alkali bath, or treatment with gases such as hydrogen chloride or nitrogen oxides, or vapors of acetic acid. All these methods may be effective in one stage of activation or another.<sup>115, 145, 146, 380</sup>

The influence of adsorbed oxygen on the catalytic activity of nickel in the hydrogenation of ethylene has been studied by Ablesowa and Zelinskaja.<sup>18</sup> The nickel wire was heated in a vacuum to the evaporation temperature and then oxygen was introduced in a uniform stream under a pressure of  $10^{-5}$  mm. The activation by oxygen is not based on the formation of a definite compound, but obviously on the change in the structure of the metal lattice at the moment of its formation. The activating action has been expressed through a curve corresponding to  $K = f(a.v/m)$ , where  $v$  is the concentration of the gas adsorbed by the layer;  $m$ , the mass of the metal, and  $a$ , a constant. The maxima of the curve are of the same order for hydrogen and oxygen. However, in the case of oxygen, the gas constant is smaller, so that the value of the action depends on the nature of the activating gas.

The configuration of metal atoms in the surface may be affected when the catalyst is subjected to these types of treatment. The transition from a crystalline to a liquid state may be brought about by melting and this, in turn, may result in a sudden decrease in the activity of the catalyst so pretreated.<sup>62</sup> Also, the chemical nature of the metals may play a significant role in producing a higher activity of the catalyst. An investigation of

the melted alloys of bismuth, palladium, cadmium, tin, and germanium at 70°F. showed that they are about five times as active as mercury, and that melted gallium is about eight hundred times as active as mercury.

Dankow and Krasnobajewa,<sup>91</sup> comparing the polymerization velocity of divinyl over thin layers of sodium obtained by condensation of sodium vapors in vacuum with the polymerization velocity of massive sodium metal, found that the polymerization velocity in the first case was 10 times higher than in the second case. This phenomenon was not interpreted as due to an increase in surface, but was assumed to be a function of increased chemical activity of the surface by the heterogeneous process of dissolution of sodium in divinyl which is related to the degree of dispersion of the thin sodium layer.

Roginsky<sup>299</sup> attempted to correlate catalytic activity with "supersaturation" in the preparation of a catalyst. He considered as "supersaturated" those systems wherein the free energy had not yet attained the minimum value and, as a measure for "supersaturation," assumed a change in free energy or in Gibbs' thermodynamic potential by transition from the given supersaturated state to the true or quasi-stable state. In catalysis, Roginsky finds that structural supersaturation is of great importance, and assumes that activation of a catalyst may be effected by contributing to it a considerable dispersion supersaturation.

If activation of a catalyst is to be interpreted as a certain type of structural distortion of the elements whose catalytic surface is only potentially active, then another activation method not yet publicized, such as electronic bombardment of the freshly prepared surface, would be applicable. Bombarding the surface of a catalyst with a stream of electrons having as their source an incandescent metal strip or filament coated with a thin layer of an alkaline-earth oxide may bring about activation. When currents driven by high potentials pass through gases at low pressures, electrons are shot out from the cathode. Electrons of a beam so obtained are able to penetrate thin sheets of metal, and these can be led out of the discharge tube when obtained through an aluminum window, as Lenard first experimented; therefore they can be conducted directly into the container where either the catalyst is pretreated or in which and over which the catalytic reaction actually takes place. It is believed that activation produced in this case corresponds to a mechanical knocking out of electrons from the catalyst surface; in other words, according to Pissarjewsky's hypothesis, this sets forth not only the desired configuration of electrons, but also brings about higher levels of energy, converting the catalyst into an active system. This may be called a type of "impulse activation" (S. Berkman).

**Reactivation.**—The activity of a catalyst changes during a catalytic reaction, either because the catalyst itself is unstable, corroded or readily aged under the conditions provided by the catalytic reaction, or because a fatigue of the catalyst takes place with the principal reaction, especially at elevated temperatures, side reactions giving rise to highly condensed, slightly volatile, carbonaceous or tarry substances which, when deposited on the active surface of the catalyst, rapidly enfeeble it.

For the restoration of the activity of the catalyst, various methods have been proposed, some employing more or less drastic measures for expelling or destroying foreign substances, thereby renewing the surface exposed to contact with the components of the catalytic system. Sometimes chemical treatment may be of service in restoring the activity of a poisoned catalyst. Sometimes it is important to regenerate the catalyst very often, depending on the number of times it has been used, thereby preventing the catalyst from losing its activity entirely and being poisoned so that ordinary methods of restoring activity are ineffective. The method of reactivation chosen is a function of the kinds of impurities which render a catalyst inactive, as well as of conditions under which inactivation takes place, and depends also on the tenacity with which the impurities are kept on the catalyst.

In general, it may be said that regeneration of worn-out catalysts involves such methods as simple mechanical cleaning of the surface; heating to the melting point; calcination in a stream of air to burn off tarry deposits; reduction at suitable temperature, the metal oxide being dissolved in appropriate acids; subjecting to a gas treatment for several hours, for example, chlorine at 200–500°,<sup>330</sup> or inert gases, such as combustion gases;<sup>188, 189, 190</sup> electrolytic treatment, such as oxidation at the anode followed by reduction in hydrogen atmosphere;<sup>331</sup> treatment with hot chemically active gases;<sup>223</sup> treatment with air at 800° followed by treatment with hydrogen chloride at about 600°.<sup>391</sup>

The possibilities for regeneration may be traced either through the individual catalyst, or the type of reaction in which the participating catalyst requires a renewal of its catalytic properties.

**Reactivation of Platinum Catalyst.**—The regeneration of platinum catalyst poisoned by mercuric cyanide is not possible by oxidation in sulfuric acid, but it may be possible in an alkaline hydrogen peroxide solution frequently renewed, or by glowing followed by additional treatment in alkaline hydrogen peroxide.<sup>248</sup> The exhausted platinum catalyst which has been used in the oxidation of sulfur dioxide to sulfur trioxide may be restored to its original activity by impregnating with water-soluble organic acids, such as acetic, benzoic, propionic, oxalic, phthalic and lactic, treating with alcohol or a volatile solvent, and heating at about 400°.<sup>172</sup>

A method has been proposed whereby spent platinum catalyst may be converted into a hydrogenation catalyst of a good quality. The glowed platinum material is dissolved in aqua regia, evaporated in hydrochloric acid and precipitated with ammonium chloride and alcohol. The ammonium chloroplatinate is reduced at red heat with carbon monoxide and the platinum obtained redissolved and used without further treatment as a catalyst. Repeated precipitation as ammonium chloroplatinate is undesirable.<sup>34</sup>

**Reactivation of Palladium Catalyst.**—An increase in the reduction temperature, using foliated palladium as a catalyst, increases the reduced particles of the surface and decreases the active surface. It has been found that long heating of pure foliated palladium up to 500–520° leads to a complete loss of permeability to hydrogen. The change takes place grad-

ually and more rapidly as the temperature is increased. In this case, the change is irreversible. Heating the foliated palladium to 450–500° does not result in a poisoning of the metal; therefore it may be regenerated or converted into states of varying permeability to hydrogen. It has been observed that heating foliated palladium, of decreased permeability to hydrogen and decreased activity, in a stream of air at 500° followed by cooling, also in a stream of air, and then reducing with hydrogen at a temperature of 140° may lead to an almost complete regeneration of permeability to hydrogen; reduction of an oxidized sample of foliated palladium at 500° causes no change. The temperature (500°) required for pure palladium may be essentially decreased in the case of commercial palladium due to the presence of certain impurities. The palladium surface may be composed of ordinary crystals or the metal may be in an amorphous state.<sup>240, 241</sup>

In studying the catalytic decomposition of hydrogen peroxide by colloidal platinum and palladium, Rocasolano<sup>295</sup> found that the catalytic action of platinum and palladium sols does not decrease at once with age; rather it increases, reaching a maximum after several days, then gradually decreasing. Rocasolano believes that the reason for the change in catalytic activity is due to a change in the oxygen concentration of the platinum and palladium sols.

Paal and Hartman<sup>265</sup> obtained evidence that palladium sol is made passive by mercury and mercuric oxide. They interpreted the anti-catalytic action of mercury and mercuric oxide to their gradual transition into the colloidal state, accompanied by a steadily progressing decrease and finally complete elimination of the adsorption ability of the palladium hydrosol to hydrogen.

**Reactivation of Nickel Catalyst.**—In hydrogenation reactions accompanied by the formation of hydrogen sulfide, nickel catalyst loses its efficiency during 4–5 weeks of operation. Treatment of the spent catalyst for one week with a carefully controlled stream of air at a gradually increasing temperature removes the carbon deposit and renders the catalyst good for another two years, providing the regeneration is periodic.<sup>118</sup> A nickel catalyst which has become inactive in the catalytic hydrogenation of fats may be regenerated by boiling with a dilute alcohol or alkali solution, or by using any substance which decreases the surface tension of water against the fatty catalyst particles, followed by washing thoroughly with an alkali sulfate and then reducing with a stream of hydrogen at a constantly rising temperature. The temperature rise should not exceed 150°C. per hour and should not exceed 650° after a period of 4–5 hours. Treatment with acid or nickel sulfate has been suggested.<sup>315, 316</sup>

Nickel borate used in the hydrogenation of fatty acids is reactivated by stirring it well with refined olive oil for  $\frac{3}{4}$  of an hour while heating, separating it from the oil and boiling with ether, then heating in the presence of hydrogen for 45 minutes at 430–440°.<sup>261</sup> The catalyst used in the hydrogenation of fats is regained by filtering it at a temperature up to 200° and under a pressure of 1–3 kg. per sq. cm. through asbestos, porcelain, or biscuit porcelain.<sup>246, 247</sup>

Metal catalysts, particularly nickel, which have partially or wholly lost their activity in the hydrogenation of fats and oils, are regenerated by heating in an autoclave under 14 atmospheres of vapor pressure, whereby the adhered fat particles are saponified by the catalyst and the catalyst precipitated from the metallic soap.<sup>77</sup> Nickel catalyst used for the hydrogenation of fats may be regained by freeing from fat as far as possible, dissolving in nitric acid, precipitating with a base, treating with formic acid, and finally decomposing the nickel formate by heating.<sup>109</sup> A nickel catalyst rendered inactive in the dehydrogenation of fats is boiled with dilute alcohol or an alkali solution without first removing all traces of organic compounds, thoroughly washed, and then reduced in a stream of hydrogen at a gradual increase in temperature.<sup>166, 167</sup> The proposal has been made to regenerate catalysts used in the hydrogenation of fats by treating them with a fat-dissolving medium and then with a reagent that will remove the oxide layer. The catalyst, after washing, should be kept from contact with air.<sup>291, 351</sup>

Zelinsky and Pawlow,<sup>322</sup> investigating the dehydrogenating ability of various catalysts, found in the case of nickel that after one application the process is accompanied by side reactions, the cyclohexane splitting into benzene and methane whereby nickel is covered with a thin layer of carbon, thereby reducing its dehydrogenation capacity. This does not take place in the case of platinum and palladium black, which are preferable as catalysts in dehydrogenation.

Richardson (Swift & Co.)<sup>368</sup> regenerates nickel catalyst by heating with a comparatively small amount of oil and hydrogen up to 200–250°, until it becomes active again.

The regeneration of catalysts, such as nickel, copper, iron, and chromium, or other heavy metals, as well as their oxides and suboxides, or their mixtures, which have lost their activity in reaction with sulfur compounds, may be carried out in one of three ways: (1) the metal contained in the mixture is converted by heating with alkali hydroxides or alkali carbonates into catalytically active compounds and freed from sulfur by washing, as sulfur is converted into the corresponding sulfate; (2) the addition of alkali and the treatment of the catalyst at room temperature instead of at increased temperature; and (3) the catalyst mass is treated at high temperature and under pressure whereby the action is spread over the side of the contact mass.<sup>46</sup>

A catalyst which has been used in the hydrogenation of oil is reactivated by heating it to 190–210° with a freshly prepared catalyst in a vessel containing oil, and the mixture obtained is passed through a tube at a temperature higher than the temperature of the oil.<sup>15</sup> Nickel catalyst poisoned by sulfur is regenerated by formic acid or acetic acid vapors led through a cooled reaction tube and the nickel formate and the nickel acetate decomposed at increased temperature.<sup>282</sup>

Walker, Russell and Marschker,<sup>402</sup> investigating the action of water on the decomposition of ethyl alcohol over nickel surfaces, ascertained that the catalysts lose their activity gradually by use, but that they may be reactivated by treatment with hydrogen at 350°.

In the hydrogenation of vegetable oils, the spent nickel catalyst may be regenerated by converting it into nickel sulfate on treatment with sulfuric acid and treating the salt with sodium acetate and iron sulfate in order to remove the compounds of phosphorus and aluminum, the precipitate separated by filtration, and the nickel isolated by converting into nickel carbonate followed by reduction with hydrogen. The nickel sulfate obtained after treatment of the spent nickel catalyst with sulfuric acid has been also mixed with kieselguhr, precipitated by sodium carbonate and the nickel carbonate reduced with hydrogen.<sup>117</sup>

Regeneration of used mixed nickel catalysts may be effected according to Etinburg<sup>116</sup> by dissolving the nickel catalyst in sulfuric acid, neutralizing on heating with sodium carbonate and adding first sodium hypochlorite and then sodium acetate in order to precipitate iron, phosphorus and aluminum.

Regeneration of nickel catalyst, prepared from nickel sulfate, nitrate, acetate, or chloride by precipitating with alkali carbonate according to F.P. 822,222, consists in passing superheated water vapor through the catalyst suspension. Thereby nickel is converted into nickel monoxide and this is reduced with hydrogen again to nickel.<sup>106a</sup>

A method has been suggested for the removal of contact poisons, such as sulfur, phosphorus, or arsenic, from the reaction vessel. In this particular case a chromium-nickel steel kettle was used in the preparation of methyl formate. The contact poisons were removed by treatment with hydrogen in the presence of iron oxide, lead oxide, or nickel acetate in benzene at 400° temperature and 200 atmospheres' pressure.<sup>129</sup>

Orlow and Brown,<sup>262</sup> studying the decomposition of thiophene in the presence of hydrogen over nickel oxide and cobaltous oxide at 400°, found that the highest desulfurization possible under these conditions was up to 78 per cent, the remaining sulfur consisting of readily removable sulfur compounds, and were unsuccessful in attempting to recover the nickel oxide catalyst after use by heating it in air and in a stream of hydrogen.

Catalysts used in the treatment of oils may be regenerated by oxidation, either by air or some other oxidizing agent. This reactivation takes place between two treatments: the first is with a saturated or supersaturated water vapor at a temperature which the treated contact mass reaches only after washing, and corresponding to the initial temperature of combustion; in the second treatment the temperature of the contact mass is reduced by washing to that required for normal treatment of the initial substance.<sup>344</sup>

The usual procedure for the isolation of nickel and the extraction of fat from a nickel catalyst, after it has been used in the hydrogenation of fats, involves placing the spent catalyst in a water bath containing sulfuric acid, boiling for eight hours by the introduction of vapor, filtering off the precipitate from the solution containing nickel sulfate, and reheating; the residue deposited contains 30 per cent fat and up to 0.6 per cent nickel.

Troyanowsky<sup>395</sup> proposed a method for the regeneration of a spent catalyst by which the catalyst mass is subjected to heat in a kettle with stirring until a uniform mixture of liquid consistency is formed, treated with an aqueous solution of sodium hydroxide, and diluted with water. The fat rises to the top of the solution and the nickel freed from the fat is treated

with sulfuric acid on heating. About 30-per cent sodium hydroxide of 20° Bé is used for every 500 kg. of spent catalyst. Nickel catalyst poisoned by desulfurization of Tschimbajew petroleum can be successfully regenerated by heating in hydrogen up to 350–400°. <sup>392</sup>

**Reactivation of Cobalt and Iron Catalysts.**—In the use of cobalt and iron catalysts for the synthesis of higher hydrocarbons from water gas at atmospheric pressure, it has been suggested that cobalt catalyst may be regenerated by heating with hydrogen up to 330° for a long period of time and subjecting iron catalyst to a stream of air at 400° followed by reduction with water gas at 260–310°. In catalytic reactions, cobalt catalysts are more active than iron catalysts and show, therefore, a correspondingly stronger hydrogenation action.<sup>49</sup> The loss in activity of a ferric oxide catalyst in a water gas reaction usually occurs very rapidly above 800° and may be completely prevented by the addition of 7 mol per cent chromic oxide; precipitation of carbon from carbon monoxide is also delayed. Yoshimura<sup>417, 418</sup> interpreted these results by assuming the formation of a solid solution between ferric oxide and chromic oxide, or by the formation of a spinel. In the preparation of ethyl chloride, the catalyst ferric chloride or aluminum chloride was regenerated by treatment with chlorine at 100°. <sup>366</sup>

**Reactivation of Mercury Catalyst.**—The regeneration of mercury sludge, obtained in the catalytic preparation of acetaldehyde from acetylene when mercuric oxide dissolved in 25-per cent sulfuric acid has been used as catalyst, is carried out by blowing the vapor of a suitable liquid into the catalyst acid sludge.<sup>400</sup> A regeneration method for mercury sludge separated out in the preparation of acetaldehyde from acetylene has been recommended by Imperial Chemical Industries, Ltd.<sup>198</sup> In this process the mercury sludge containing the silver and iron salts is separated from the aqueous solution, dissolved in concentrated nitric acid, and sulfuric acid added. The mercury sulfate obtained is mixed with iron sulfate and used in dilute sulfuric acid for the hydration of acetylene.

**Reactivation of Copper Catalyst.**—It has been stated by Irlin<sup>209</sup> that in large-scale production of aniline from nitrobenzene, using a mixture of copper and 10-per cent calcium oxide at 240–250°, the catalysts may be readily regenerated if prepared from their nitrates by heating for 3–4 hours at 350° and reducing for 12 hours at 300° in a hydrogen atmosphere.

Waste products of copper and copper alloys in the presence of cupric chloride catalyst may be converted with sulfuric acid and oxygen into copper sulfate.<sup>7</sup> The catalyst regenerates readily, according to the equation:  $\text{CuCl}_2 + \text{Cu} \longrightarrow \text{Cu}_2\text{Cl}_2$ ;  $\text{Cu}_2\text{Cl}_2 + \text{O} \longrightarrow \text{CuO} + \text{CuCl}_2$ . Catalysts consisting of copper mixed with activators and used for the dehydrogenation of alcohols to form esters may be regenerated by melting them together with aluminum. It has been ascertained that after removal of aluminum the catalyst shows even a higher activity than that of the original material. For example, a catalyst formed by fusing copper or copper alloy with a corresponding catalyst and rendered inactive may be regenerated when mixed with an equal amount of aluminum in a graphite crucible at 600–800° and extracted on a water bath with 10 per cent sodium hydroxide. A



copper catalyst containing 0.9 per cent zirconium regenerated in this manner and used in the catalysis of ethanol at 250–275° gave 53 per cent ethyl acetate and in the catalysis of butanol, 40 per cent butyl butyrate; after 78 hours' exposure, the activity decreased 7 per cent. A similar behavior has been ascertained for a regenerated copper catalyst containing 0.2 per cent cerium. Pure copper pretreated gave 40–50 per cent ethyl acetate at 250–270°. <sup>96</sup>

Catalysts used in the splitting of mineral oils containing 0.5–1.5 per cent salts of manganese, nickel, cobalt, iron, copper, or chromium, when subjected to an oxidative regeneration, favor the combustion of carbon formed on the contact mass. <sup>191</sup> A copper catalyst used in the dehydrogenation of ethanol at 300°C. becomes coated with condensation products which lower its activity. The activity of the catalyst may be restored by oxidizing the organic material with hot air followed by reduction of the metal oxide with alcohol. <sup>323</sup>

#### **Reactivation of Zinc, Chromium, Molybdenum and Tungsten Catalysts.**

—In the preparation of methanol and other oxygen-containing organic compounds zinc and chromium oxides, obtained by heating a mixture of zinc and chromium carbonates, may be used. When alkali salts are present, these catalysts may be used in the preparation of higher alcohols. In case the activity of the catalyst ceases, the contact mass is regenerated by heating up to 300–400° in a stream of air or oxygen, or dissolving in sulfuric acid and precipitating with sodium carbonate and heating. <sup>202</sup>

In the reactivation of catalysts used in the hydrogenation of hydrocarbon oils, particularly those containing chromium, molybdenum, or tungsten compounds and sulfo-active, most of the oil is separated from the contact mass and the latter subjected for a long period of time to the action of a gas containing free hydrogen and substantially freed from hydrocarbons. <sup>357</sup>

Kelber <sup>215</sup> regenerated chromium oxide salt used in the preparation of ethylene from acetylene by reduction. Saturated hydrocarbons are dehydrogenated at about 500° to olefinic hydrocarbons over bi- or trivalent chromium used with or without a carrier. The catalyst is claimed to be very stable, but if necessary may be readily reactivated by prolonged heating at 550° in the presence of hydrogen. <sup>348</sup>

In catalysts containing chromium and molybdenum, the molybdenum may be recovered if the catalyst is oxidized and then treated with a solution of ammonium sulfide containing free ammonia. The amount of ammonium sulfide is such that the total molybdic acid passes into solution as ammonium sulfomolybdate, the chromic acid being insoluble. After filtration, lead oxide is added to convert the ammonium sulfomolybdate into the molybdate; the solution is then refiltered, and molybdic acid is precipitated with hydrochloric acid; lead sulfide is converted by oxidation into the oxide and re-used. <sup>130</sup>

The recovery of molybdenum from petroleum hydrocarbons may be carried out by heating the hydrocarbon residue with fuller's earth, diatomaceous earth, or bentonite, and driving out the volatile products. A

repetition of this process increases the amount of molybdenum recovered which is treated with a suitable solution.<sup>261</sup>

Bahr and Petrick,<sup>29</sup> studying the catalytic reduction of tarry phenols to cyclic hydrocarbons over molybdenum trioxide at 360–380°, found the most active catalyst to be molybdenum trioxide-chromic oxide-barium oxide in the ratio of 1 : 1 : 10, and the best carrier, kieselguhr. The tendency of molybdenum trioxide to become inactive when used at atmospheric pressure has been attributed to the formation of the less active molybdenum dioxide rather than to the formation of high-boiling compounds in the reaction. Satisfactory regeneration of the molybdenum trioxide catalyst was obtained by treatment with air, but not with kieselguhr as a carrier. The use of ammonia in the reactivation process poisoned the catalyst, and hydrogen sulfide gave no better result over hydrogen.

In order to regenerate molybdenum and tungsten from contact masses used in the pressure hydrogenation of fuels, it is recommended that they be oxidized at 425–480°, thereby converting the sulfides into the oxides; molybdenum trioxide is extracted from the contact mass by dilute hydrochloric acid, and precipitated by the addition of ammonia, maintaining a slightly acid condition. The insoluble tungsten trioxide remaining after treatment with hydrochloric acid is dissolved in concentrated ammonia and purified by a second precipitation.<sup>204</sup> A similar method for the regeneration of molybdenum-containing catalyst has been patented by the Standard I. G. Co.,<sup>360</sup> namely, the catalyst is subjected to oxidation, treated with an acid solution (hydrochloric acid to which nitric acid has been added), neutralized with ammonia, and the precipitated molybdenum oxide combined with alkaline earth salts, oxides of rare earths, asbestos, and other substances.

**Reactivation of Catalysts Active in Hydrogenation Reactions.**—The spent, inactive catalyst is regenerated by boiling with an acid in which it dissolves, precipitating with an alkali, washing, and heating slowly up to 650° in a stream of hydrogen. It has been suggested that the increase in temperature should not exceed 150° per hour and should be uniform for at least 4–5 hours.<sup>317, 318, 319, 320</sup> Catalysts used in the hydrogenation of oils were treated with acids while being heated, and then filtered; their catalytic properties were thus renewed.<sup>187</sup> To remove a magnetic catalyst from a hydrogenated oil, the use of a magnet and filtering off<sup>112</sup> are suggested.

A method eliminating the regeneration of metal catalysts used in the catalytic hydrogenation of oils and fats has been patented by Bolton and Lush.<sup>55</sup> By adding mono- or diglycerides of fatty acids to oils, the precipitation of metal soaps, which reduce the activity of the catalyst, is prevented and hydrogenation accelerated.

In the preparation of nitrogen oxides from hydrogen mixtures, the regeneration of catalysts used may be effected by washing with a dilute alkali solution.<sup>8, 268</sup> Reactivation of sulfide catalysts of the sixth group, used for the hydrogenation of fuels, is made possible by washing with solvents to reduce the viscosity and to remove adhering particles of hydrocarbons and by treating with a vaporized mixture of ammonia and water under 20–100 atmospheres' pressure.<sup>362</sup> Regeneration of pressure hydro-

generation catalysts consisting of metal sulfides of the sixth group, together with those of the second and fourth groups of the periodic system of elements, may be carried out by freeing them of adhering particles of hydrocarbons, washing with carbon disulfide, digesting with 6*N* hydrochloric acid at ordinary temperature with the addition of small amounts of nitric acid, washing with hydrochloric acid and water, and drying. The precipitated sulfides of the sixth group are mixed with magnesium oxide and molded into briquettes. These are very active catalysts.<sup>359</sup> Catalysts (sulfides of the sixth group) for pressure hydrogenation are reactivated by subjecting them to the action of gases containing 2–25 per cent of oxygen by heating at slowly increasing temperature for 2–5 hours.<sup>363</sup>

Adsorbed halide compounds, especially those containing elements of the sixth group, such as molybdenum, used as hydrogenation catalysts, may be regenerated by the addition of gaseous substances which form volatile compounds with the halides, and subsequently removing them, for example, water vapor and hydrogen, carbon monoxide and hydrogen, or sulfur dioxide and hydrogen. With the addition of hydrogen sulfide, these catalysts are active at temperatures between 500 and 1000°F.<sup>358</sup>

Sulfo-active catalysts for the hydrogenation of hydrocarbons are reactivated by separating the impurities from the catalyst and treating with a gas containing free hydrogen with elimination of hydrocarbons at pressures of about 50 atmospheres.<sup>205</sup>

Tupholme<sup>296</sup> proposed hydrogenating oil in a continuous process using a fixed catalyst instead of distributing it in the form of a suspension in the reaction products. In this process the oil and hydrogen are passed over the catalyst, and the continuously flowing hydrogenation product is filtered. Under these conditions, the catalyst may be readily regenerated, thus insuring long life without serious loss.

A so-called intermittent regeneration of a catalyst used in the hydrogenation of polymer olefinic hydrocarbons, for example, diisobutylene to isooctane, may be carried out by passing a hydrogenation charge containing contact poisons over a catalyst until the activity of the catalyst has been decreased by 5–30 per cent, then leading the poison-free hydrogenation charge over the catalyst until the activity of the catalyst has been restored, when it is recharged with the poison-containing hydrogenation charge. In case the initial hydrogenation charge is free from poison, a poison-containing hydrogenation gas, such as sulfur, may be used; in the regeneration interval this is combined with the poison-free hydrogenation gas.<sup>207</sup>

Regeneration of pressure hydrogenation catalysts, such as molybdenum sulfide catalyst, is carried out by heating to a temperature not above 750° in the presence of air, then dissolving in about 50-per cent sulfuric acid, diluting the solution to an acid content of 20 per cent, and precipitating molybdenum trisulfide. The molybdenum trisulfide is filtered and dried with elimination of air in an inert or reducing atmosphere.<sup>358a</sup>

**Reactivation of Catalysts Active in Oxidation Reactions.**—Catalysts used in the oxidation of organic compounds by oxygen may be regenerated by treatment with nitric acid in which the oxides are soluble.<sup>39</sup> The reactivation of contact agents in the preparation of nitrogen oxides has

been effected by washing with an alkali solution.<sup>8</sup> Catalysts, especially those containing one or more metal oxides, rendered inactive in the preparation of methanol or other similar organic compounds may be reactivated by treating with hydrogen or hydrogen-containing gases at temperatures approximating those at which the catalyst is active. In the regeneration of catalysts which have been used in oxidation and reduction processes, the gases used for treatment are filled in tubes arranged in the form of perforated rings which serves to facilitate their dispersion when dipped into the contact mass, whereby the catalyst action is restored.<sup>190</sup>

Swiss patent No. 154,174 (1932) describes a method for obtaining phenol from chlorobenzene by passing the latter over magnesium chloride precipitated on silica gel in the presence of water vapor at 400–700°. The fatigue of the catalyst in this reaction is attributed to the deposition of carbon and the conversion of the basic oxide of the catalyst into a silicate. The method of regeneration of this catalyst has been described in two German patents,<sup>160, 161</sup> in the first of which blowing chlorine mixed with other gases through the contact mass at high temperatures is proposed; in the second, air is used.

Tischenko, Gutner, Schigelskaja and Faerman<sup>391</sup> recommended the following methods of regeneration: (1) blowing air or oxygen through the spent catalyst at a temperature not higher than 800° until the disappearance of carbon dioxide in the outlet gases and following this by the introduction of gaseous hydrogen chloride at a temperature not exceeding 600° for from 30 minutes to 2 hours; and (2) blowing a mixture of chlorine and water vapor through a spent catalyst until complete combustion of carbon takes place at a temperature not higher than 800°.

Kaschtanow and Ryshow,<sup>213, 214</sup> studying the oxidation of sulfur dioxide by oxygen in the presence of bivalent manganese, found that the accumulated sulfuric acid poisons the manganese sulfate catalyst and that it is rendered wholly inactive in a 20-per cent sulfuric acid solution. Furthermore, the investigation of the oxidation of sulfur dioxide by ozone showed that the reaction velocity increases with decrease in the concentration of oxygen and increases with an increase in the concentration of sulfur dioxide in the initial gas. The addition of phenol does not influence the oxidation process, and in the presence of sulfur dioxide, oxygen shows no regenerative effect on the poisoned manganese sulfate. The increase in the reaction velocity, although at 40°, in the presence of phenol, indicates a "partial" regeneration of the manganese salt. The phenol itself may poison the catalyst due to the formation of manganic acid. On the other hand, the aqueous phenol may be oxidized to quinone as an end product, which has no poisoning effect on the catalyst.

Siegert<sup>333a</sup> claims that vanadium pentoxide catalyst poisoned with arsenous oxide (in the catalytic oxidation of sulfur dioxide by air to sulfur trioxide) may be regenerated and improvement of the activity achieved by using higher streaming velocities (up to 60 liters per minute), as well as by temperature increase. A strong increase in the oxidation velocity with temperature observed at higher temperatures is considered as an indication of the decrease in the poisoning phenomenon.

The inclusion of the regeneration of catalysts poisoned by individual contact poisons is unavoidable in a systematic study of the regeneration of catalysts as a whole. A few methods have been recommended for regenerating catalysts poisoned by sulfur. One of these is to subject them in a dry state to the action of vapors of organic acids, such as acetic and formic, by introducing them into the catalyzing apparatus after cooling the catalyst to 100°, whereby the contact mass is converted into the metal itself by decomposition of the organic salt formed by an increase in temperature.<sup>162</sup>

The Compagnie Internationale pour la Fabrication des Essences de Pétrole<sup>84</sup> patented an apparatus suitable for the regeneration of sulfurized catalysts by the use of air. Metal oxide catalysts, used in the hydrogenation and cracking of high-boiling hydrocarbons, on which carbon has been deposited and which have been poisoned by sulfur may be regenerated with a mixture of air or oxygen and water vapor in such a manner that carbon is removed in the form of carbon monoxide or carbon dioxide and sulfur as hydrogen sulfide without the formation of sulfates.<sup>85</sup>

The role of sulfur in destructive hydrogenation has been discussed by I. G. Farbenindustrie A.-G.<sup>143</sup> and Szeszich and Hupe,<sup>372</sup> who recommend adding iron oxide to combine with the sulfur to offset its effect in the high-pressure hydrogenation of coal or tar by the Bergius method. On the other hand, in some cases, the amount of sulfur present in the reaction system influences favorably the yield of reaction products. Klever showed the advantage of using so-called sulfur-fast catalysts and Vargu called attention to the importance of sulfur in the case of molybdenum, tungsten, iron, nickel and cobalt catalysts. Szeszich and Hupe actually determined the increase in the yield of benzene, up to 44 per cent, using a definite amount of sulfur or sulfur-containing compounds. It has been found that the formation of oil is decreased in favor of the benzene yield by the addition of sulfur. Therefore, the regeneration of catalysts by the removal of sulfur or sulfur-containing compounds is not always desirable because at times, in some particular catalytic reaction or under definite physical conditions, sulfur may be the activating agent.

In order to facilitate the regeneration of a catalyst deposited on an aluminum silicate carrier, used in the hydrogenation of hydrocarbons within a temperature range 482–538°, and the combustion of carbon and sulfur accumulated, it has been suggested that 0.1–1.5 per cent metal oxide of manganese, nickel, cobalt, or copper, or their compounds, molded in a cylindrical form 2 mm. high and 2 mm. in diameter, be added and the mixture subjected to periodic oxidation.<sup>345</sup>

Removal of sulfur compounds from gases may be carried out by the use of catalysts. For the hydrogenation of organic sulfur compounds in hydrogen sulfide, oxides of nickel, molybdenum, or chromium impregnated to the extent of 20 per cent on a carrier consisting of a large-pore hydroxide gel having a density of 0.5 and a grain size of 1.16–2.32 mm. (retards adsorption of water at 30° temperature and 22 mm. pressure) dipped into a calcium chloride solution of such a concentration that the dried gel contains 35–40 per cent of this salt, may be used. After dipping, the gel is dried,

washed with hot water, re-dried, and activated by heating before it is impregnated with the metal oxide catalyst. If sulfur is removed by oxidation, oxides of iron, aluminum, or vanadium may be used.<sup>367</sup>

A catalytic method has been proposed<sup>57</sup> for the removal of poisons from manufactured gas in which the hot reacting substance is inserted between the contact chamber and the chamber in which the reactivation of the catalyst actually takes place. This process is continuous and operates in a closed circuit. The regeneration of sulfur in the form of solid compounds is brought about by the addition of ammonia and water in a vapor state to the outlet gas. In the reaction between sulfur dioxide, ammonia and water vapor according to the reaction:  $2\text{NH}_3 + \text{SO}_2 + \text{H}_2\text{O} \longrightarrow (\text{NH}_4)_2\text{SO}_3$  and  $\text{NH}_3 + \text{SO}_2 + \text{H}_2\text{O} \longrightarrow \text{NH}_4\text{HSO}_3$ . Complete precipitation takes place at room temperature.<sup>245</sup>

The removal of sulfur dioxide from gases may be carried out by washing with an aqueous solution of organic bases containing inorganic compounds such as the oxides, hydroxides, or carbonates of the alkali metals, or of magnesium, which reacts with the sulfates of organic bases, forming inorganic water-soluble sulfates. The adsorbed sulfur dioxide is driven off by heating the wash solution.<sup>17</sup>

Catalysts used in the removal of nitrogen oxides from gaseous mixtures may be regenerated by treating with aqueous ammonia or a dilute solution of the hydroxides, carbonates, or sulfohydrates of the alkali metals.<sup>9</sup> This method is similar to that proposed by the Société Européenne de l'Ammoniaque.<sup>341</sup>

As an improvement for the direct regeneration of gases or vapors or their mixtures with catalysts or other purifying substances, it is recommended<sup>83</sup> that they be conducted through a series of long tubes to single distribution tubes immersed in the catalyst or purification agents. These long pipes may have an outlet in a collecting tube.

It may be of interest to note a few facts directly or indirectly connected with the problem of regeneration which could not logically be inserted under any of the respective headings.

Catalysts used in the preparation of secondary amines from primary amines, for example, by passing aniline vapors (250 g. per hour) over aluminum oxide or titanium oxide heated to 450°, may be regenerated by heating in a stream of air.<sup>71</sup>

Brown and Travers<sup>59</sup> have shown that the removal of hydrogen from carbon takes place rather slowly when carbon is saturated with hydrogen at 740°. Degassing requires about 48 hours, but as soon as methane is introduced, it is possible to recover the hydrogen partly as methane and partly in the uncombined state. This has been interpreted by Nyrop from his adsorption viewpoint on catalysis, that is, methane has a lower energy of ionization than hydrogen. Methane is ionized at 13.70 volts and hydrogen at 15.37 volts (refer to chapter on Contact Catalysis).

Standard Oil Co. (Indiana)<sup>364a</sup> regenerates catalysts, such as double chlorides,  $\text{NaAlCl}_4$ ,  $\text{LiAlCl}_4$ ,  $\text{SbAlBr}_6$ ,  $\text{HgAl}_2\text{Br}_8$ , used in the cracking of hydrocarbons, in the desulfurization of hydrocarbons, or in the polymerization of gaseous olefins, by treating them in a melted state at about 375° to

825° with chlorine or bromine. The regeneration may be carried out in such a manner that the fresh catalyst flows through the reaction zone where it becomes contaminated with high molecular weight impurities, after which it goes to a regeneration chamber where it flows in a stream counter-current to the halogen. After regeneration the catalyst is returned to the reaction zone.

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## Chapter 5

### Inhibitors in Catalysis

According to the present conception of catalysis a catalyst may affect a chemical reaction either by increasing or by decreasing its velocity. Furthermore, the speed of the catalyzed reaction may be altered by the addition of small amounts of secondary agents. It is therefore desirable to differentiate carefully between the various types of catalytic behavior.

A catalyst which accelerates a chemical process is designated as *positive*. *Negative catalysts*, on the other hand, decrease the velocity of a reaction. A *promoter* is a substance which improves the action of the primary catalyst, and tends to further its effect; an *inhibitor* has a preventive action on the catalyst and tends to nullify its effect. Promoters and inhibitors are secondary agents; they function in the presence of primary catalysts, either positive or negative, and their activity must be measured with reference to the effect of the primary catalyst.

Considerable difficulty is experienced in a strict classification of catalytic phenomena due to changes not only in the physical and chemical nature of the catalyst, promoter, or inhibitor, but also in the conditions under which the reaction sometimes proceeds. There are also factors which influence the process greatly, but are not readily traceable. For example, traces of water, dust particles, foreign bodies, or changes in the medium in which the catalytic reaction proceeds may be of great importance, although their effect cannot readily be evaluated. Reactions which occur in anhydrous organic solvents or 100 per cent sulfuric acid are often inhibited by traces of water. In heterogeneous systems, the inhibitory effect is often related to the catalytic activity of dust particles or films on the walls of the container.

The addition of a small quantity of water greatly decreases the rate of many reactions which take place in anhydrous media, especially those occurring in absolute alcohol, for example, esterification of acids,<sup>56</sup> the alcoholysis of amides<sup>118</sup> and the formation of a lactone from a hydroxy acid.<sup>68</sup> A small quantity of water also decreases the rate of decomposition of oxalic acid<sup>23</sup> in 100 per cent sulfuric acid. The effect of traces of moisture may be explained<sup>130</sup> by assuming a displacement of the internal equilibrium which, thermodynamically interpreted, implies that a large amount of work is necessary to withdraw the last traces of water from a substance.

On the other hand, small amounts of impurities or traces of water may be essential to many reactions.<sup>43</sup> It has been stated<sup>136</sup> that absolutely dry mixtures of carbon monoxide and oxygen cannot be exploded, and that a flame of carbon monoxide can be extinguished by very dry air. The presence of moisture greatly depresses the emission of infrared radiation from exploding carbon monoxide-oxygen mixtures and increases the rate

at which thermal equilibrium is reached. The direct reaction of water with carbon monoxide<sup>4</sup> as well as the fact that dry hydrogen and oxygen do not combine even at 1000°<sup>8</sup> has been disproved.

Experimenting with the oxidation of nitric oxide, which was studied kinetically by Bodenstein,<sup>17</sup> Baker<sup>9</sup> and Briner<sup>25</sup> showed that although traces of moisture catalyzed the reaction at ordinary temperatures, the velocity of the homogeneous reaction was greatest at liquid air temperatures, at which the concentration of water vapor is extremely small. Hydration or solvation phenomena, resulting from the addition of water in an amount somewhat larger than the traces previously discussed, may increase the complexity of some catalytic processes taking place in alcoholic solutions. This has been observed in the esterification of acids<sup>77</sup> and the decomposition of diazo esters.<sup>24</sup>

There are examples<sup>53</sup> of the inactivation of a reaction by traces of substances, such as dust particles, which spread over the active areas and adhere to the walls of the vessel like a film.<sup>28, 119</sup> On the other hand, dust particles may act as catalysts, as is the case in the decomposition of hydrogen peroxide<sup>114, 115</sup> and in the thermal decomposition of nitrogen pentoxide.<sup>116</sup> Reactions of auto-oxidation (oxidation by gaseous oxygen) have been attributed in some cases to the positive catalytic action of minute amounts of impurities on the walls of the reaction vessels;<sup>97</sup> in other cases they appear to be autocatalytic. There are many examples both of organic reactions, such as the oxidation of benzaldehyde by air, and of inorganic reactions, such as the decomposition of hydrogen peroxide or the oxidation of sodium sulfite by dissolved oxygen,<sup>134</sup> which are inhibited by traces of various substances. Some investigators do not believe that those traces affect the reaction velocity.<sup>27</sup>

### Mechanism of Catalytic Inhibition

The early investigators in the field of inhibited catalysis<sup>81, 134</sup> postulated that an inhibitor suppresses the activity of a positive catalyst present in the reaction by the formation of a complex. Inhibition in this sense implies that the medium is not entirely free from positive catalysts\*; it is related to the induction phenomenon<sup>120</sup> exhibited by nickel and cobalt hydroxide catalysts with sulfites and oxygen. Catalytic inhibition for concentrated solutions of sulfites has not been proved.<sup>91</sup>

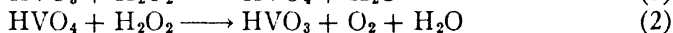
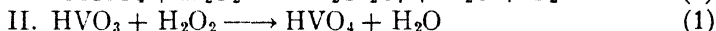
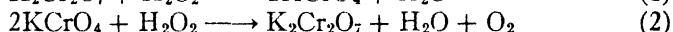
The neutralization of traces of positive catalysts<sup>84</sup> appeared to be another interpretation of the action of an inhibitor. This is opposed to the viewpoint that the inhibitor, instead of suppressing the action of a positive catalyst, interacts with just one of the components of the system, forming intermediate compounds.<sup>37</sup> This postulate does not exclude the formation of addition or adsorption compounds with reducing agents such as sodium sulfite, benzaldehyde, acrolein, or turpentine.

Ostwald,<sup>105</sup> who advanced the theory of intermediate compound formation in positive catalysis, could not explain the catalytic retardation in

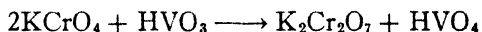
\* Titoff found that the presence of  $10^{-12}$  *N* copper sulfate solution was sufficient to accelerate the rate of oxidation of an aqueous solution of sodium sulfite and that, in spite of the infinitesimal amount, many inhibitors could suppress its action.

the same manner. Taylor<sup>132</sup> assumed the formation of a double compound by a temporary union of the inhibitor with the reactant, with subsequent dissociation to the inhibitor and the reactant, as a mechanism of inhibited catalysis. The part played by the inhibitor was designated as that of a "competitor" of a reactant. Taylor's views were supported by Underwood<sup>139</sup> who attempted also to relate the formation of a double compound and the inhibition effect.

Another mechanism conceives inhibited catalysis to be a modification of ordinary positive catalysis in the sense that it slows down the rate of the main reaction by the participation of at least one of the reactants in a more rapid side reaction with the inhibitor. In the case of the inhibited reaction, the intermediate compound regenerates the reactant and the inhibitor. In the case of positive catalysis, the intermediate breaks down into the catalyst and the reaction product. Further development of this concept leads to the conclusion that a reaction rate may be considerably decreased by a change in the reaction path due to the formation of two intermediate compounds, one of which is less reactive than the other.<sup>121</sup> This hypothesis is illustrated by an example discussing the combined influence of potassium dichromate and vanadic acid upon the catalytic decomposition of hydrogen peroxide. Vanadic acid is found to decrease greatly the rate of the reaction, which proceeds as follows:



Reaction I proceeds rapidly, followed by II. Pervanadic acid is more slowly acted upon by hydrogen peroxide than perchromic acid and the retarding effect increases as the concentration of vanadic acid increases. It is assumed that the retardation approaches a limiting value when the perchromic acid is converted into potassium dichromate and vanadic acid into pervanadic acid:



The mechanism for the inhibition of the dissociation of oxalic acid dissolved in concentrated sulfuric acid, by which a compound is formed either with sulfuric acid or oxalic acid on the addition of water, was given by Bredig and Lichty and by Christiansen.<sup>32</sup> However complete the reaction may be between the acid and the water, the presence of a small amount of water does not appreciably alter the concentration of either the oxalic acid or the sulfuric acid. It was shown, however, that if reaction between oxalic acid and sulfur trioxide takes place, the reaction will be controlled by the concentration of water due to a displacement in the equilibrium:  $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{O} + \text{SO}_3$ . It was found<sup>22</sup> that the addition of one per cent sulfur trioxide to 100 per cent sulfuric acid greatly increases the reaction velocity.

Since the protective colloids constitute a special class of inhibitors, an explanation of the inhibitory effect of these substances was proposed. The

inhibition by substances, such as gelatin, of the catalytic decomposition of hydrogen peroxide by colloidal platinum has been interpreted<sup>10</sup> by assuming that although gelatin increases the degree of dispersion of the catalyst, resulting in a larger surface of an increased catalytic activity, this effect is offset by the action of the gelatin itself, as its presence hinders the adsorption of hydrogen peroxide. This argument has been criticized by Iredale<sup>63</sup> on the basis that there is no evidence proving that protective colloids increase the degree of dispersion of a metallic colloidal solution already formed; on the other hand, Rusznyak's work<sup>123</sup> indicates a decrease in catalytic activity with an increase in dispersion, and Iredale's study reveals that the stronger the protective properties of the colloidal substance the greater its inhibitory action with respect to the catalytic activity.

The inhibition effect of protective colloid-inhibitors was explained<sup>63</sup> on the basis that selective adsorption results in a decrease in the concentration of hydrogen peroxide at the catalyst surface, which in its turn decreases the velocity of the process. In agreement with this explanation is the fact that a protective colloid hinders the adsorption of ions which induce coagulation. If the adsorption of hydrogen peroxide by the catalyst is hindered, the velocity of the reaction is retarded; obviously a strong protective colloid hinders the adsorption of ions more readily than a weak protective colloid, and therefore affects the catalytic reaction to a greater extent. The changes in the rate of decomposition of hydrogen peroxide have been ascribed also to the diffusion factor<sup>117</sup> (the rate of diffusion of the reactants to the colloid surface) as opposed to the idea of a colloid-complex formation. But from this point of view, no explanation is given for the fact that a strong protective colloid inhibits the reaction more than a weak one.

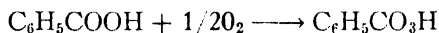
The action of an inhibitor has also been explained on the basis that it breaks reaction chains<sup>32</sup> in a system. According to the chain theory, when two reacting molecules combine, the resulting substance activates the reactants on collision. This is the beginning of the chain reaction. The rate of the chain reaction is considered to be proportional to the number of chains formed per second, multiplied by the number of links in each chain. The number of chains is a factor that may be derived from the equation  $V = Se^{\frac{-Q}{RT}}$ , in which  $S$  denotes the number of collisions for the molecular gas, and  $Q$  the mean difference between the energy of the reacting and non-reacting pairs of molecules. Whether this factor is dependent on the presence of molecular fragments is not known, but it is believed that the number of links depends on the probability of a break in the chain. The latter may be changed by an admixture of small quantities of a foreign gas the molecules of which are able to take up energy from the activated molecules or to react with them in some manner. When the inhibitor breaks the chains formed in the system, the energy of the "active"\* molecules is dissipated on colliding with it. Consideration of the catalytic process as a chain reaction, and of positive catalysts as acting by virtue of forming new active centers led to the conception of the

\* Christiansen termed *active* molecules "hot" molecules.



contrary action of an inhibitor or a negative catalyst as a deactivation of one member of the chain which thereby discontinues its course.<sup>124</sup> Recently Staveley and Hinshelwood,<sup>130a</sup> studying the thermal decomposition of acetaldehyde and propionaldehyde, proved that short chains (the average length about 2 units) occur only in the case of propionaldehyde. These chains possibly have their origin in the activation of the ethyl group and are inhibited by nitric oxide. Acetaldehyde, having molecules of slightly smaller activation energy, forms no free radicals or chains, and nitrous oxide has no inhibiting effect.

Stephens<sup>130b</sup> postulated that the direct oxidation of olefins and that of paraffin hydrocarbons probably proceeds with the initial formation of a reactive addition product with a molecule of oxygen. For instance Brunner and Rideal<sup>126a, 26b</sup> have shown that the direct oxidation of *n*-hexane exhibits an induction period analogous to that found by oxidation of benzaldehyde to benzoic acid,



perbenzoic acid ( $\text{C}_6\text{H}_5\text{CO} \cdot \text{O} \cdot \text{OH}$ ) being the intermediate compound.<sup>139a</sup> Thus in the detonation of petroleum-oxygen mixtures, an unstable peroxide is formed at isolated centers of activation, which is capable of activating the subsequent reaction by a chain process of transmission of energy. Mikhailova and Neiman<sup>90a</sup> found that the oxidation velocity of cracking benzene is proportional to the size of the contact surface of benzene and to the oxidizing gas. With the increase of the  $\text{O}_2$  partial pressure the induction period is shortened. The action of inhibitors is found to be proportional to their concentration; thus they are not adsorbed on the surface of the liquid. It is concluded that the action of inhibitors is based on the discontinuation of the reaction chains within the liquid. The fact that chain reactions are actually involved is derived from a simple calculation that the oxidation velocity is about 1,000 times greater than that corresponding to the possible number of active centers.

The inhibitors retard auto-oxidation as well as resin formation. Bäckström<sup>5a, 5b</sup> succeeded in demonstrating directly the chain character of the process studied by Moureu and by Titoff. He showed that in the auto-oxidation of aldehydes as well as of sulfite the quantum yield of several thousands may be greatly reduced by the addition of inhibitors. Insofar as substances that inhibit the photochemical chain are the same as those which inhibit the dark reaction, Bäckström assumed that the dark reaction is also a chain process.

The velocity of the dark reaction for sulfite auto-oxidation was found to obey the equation:

$$V_d = \frac{K[A]}{K_1[A] + K'[Inh.]}$$

which is the form expected for the inhibition of a chain reaction. ( $K$  and  $K'$  are considered to be a combination of velocity constants and oxygen concentration.)

In Fig. 1 is shown the inhibition of the auto-oxidation of sulfites by benzyl alcohol. The upper curve corresponds to the velocity of oxidation

of the alcohol according to the chain theory, while the lower is the one obtained by analysis.

As in conjugated chemical reactions, so in catalysis the participating components are differentiated as *actor* (oxygen in oxidation reactions); *inductor*, a substance which reacts with the actor in the primary or more rapid reaction; and the *acceptor*, which participates with the actor in the secondary, induced reaction. The difference between accelerated conjugated chemical reactions and the catalytic reactions consists in the fact

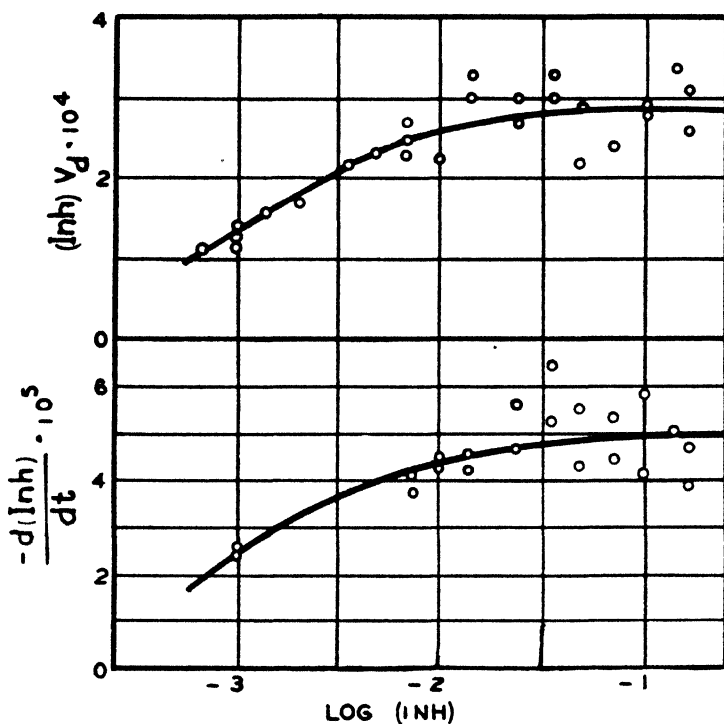


FIGURE 1.—Inhibition of the Auto-oxidation of Sulfites by Benzyl Alcohol. Upper curve shows velocity of oxidation of the alcohol, according to the chain theory; the lower shows the same, by analysis (Backström).

that the first are characterized by stoichiometric relations, while in true catalysis the induction factor is greatly increased, approaching infinity. This corresponds to a considerable decrease in the amount of the additional substance with respect to the reacting substance. Thus, whenever the induction factor has high values, it indicates that parallel to the conjugated reaction a catalytic process takes place. Table 1 is an illustration of negative catalysis proceeding parallel to conjugated reactions. For instance, a conjugation is observed between extremely slow oxidation of potassium arsenate by oxygen and oxidation of cerium salts, or a slow oxidation of indigo by oxygen and oxidation of turpentine or benzaldehyde. Turpentine and cerium salts play the part of inductor, while indigo or potassium arsenate is the acceptor.

From the viewpoint of chain reactions, it is emphasized<sup>81</sup> that the induction factor may be great if the transition of single molecules at the beginning of the many-membered reaction chain is carried out by the molecules of the reacting substance. The change in the length of such reaction chains is then expressed in a corresponding change of the induction factor.

If the catalytic properties of an oxidation catalyst are related to its susceptibility to oxidation, as has been suggested by Moureu and Dufrasse,<sup>93, 94</sup> who carried out the majority of investigations to be discussed, then, under certain conditions, the same catalyst may accelerate or retard the reaction, *i.e.*, act either as a pro-oxygen or as an anti-oxygen. The supporting evidence for this appeared to be the fact that very often the

Table 1. (Dhar and Mittra.<sup>38</sup>)

Primary Reaction	Secondary Reaction	Actor	Inductor	Acceptor
HgCl <sub>2</sub> + Na <sub>2</sub> SO <sub>3</sub>	HgCl <sub>2</sub> + Na <sub>3</sub> AsO <sub>3</sub>	HgCl <sub>2</sub>	Na <sub>2</sub> SO <sub>3</sub>	Na <sub>3</sub> AsO <sub>3</sub>
H <sub>2</sub> Cl <sub>2</sub> + H <sub>2</sub> COOH	H <sub>2</sub> Cl <sub>2</sub> + Na <sub>3</sub> AsO <sub>3</sub>	HgCl <sub>2</sub>	H <sub>2</sub> COOH	Na <sub>3</sub> AsO <sub>3</sub>
HgCl <sub>2</sub> + Na <sub>3</sub> PO <sub>3</sub>	H <sub>2</sub> Cl <sub>2</sub> + Na <sub>3</sub> AsO <sub>3</sub>	HgCl <sub>2</sub>	Na <sub>3</sub> PO <sub>3</sub>	Na <sub>3</sub> AsO <sub>3</sub>
HgCl <sub>2</sub> + Na <sub>2</sub> SO <sub>3</sub>	HgCl <sub>2</sub> + H <sub>2</sub> AsO <sub>3</sub>	HgCl <sub>2</sub>	Na <sub>2</sub> SO <sub>3</sub>	H <sub>2</sub> AsO <sub>3</sub>
HgCl <sub>2</sub> + Na <sub>3</sub> PO <sub>3</sub>	HgCl <sub>2</sub> + H <sub>2</sub> AsO <sub>3</sub>	HgCl <sub>2</sub>	Na <sub>3</sub> PO <sub>3</sub>	H <sub>2</sub> AsO <sub>3</sub>
Na <sub>2</sub> SO <sub>3</sub> + air	NaNO <sub>2</sub> + air	air	Na <sub>2</sub> SO <sub>3</sub>	NaNO <sub>2</sub>
Na <sub>2</sub> SO <sub>3</sub> + air	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> + air	air	Na <sub>2</sub> SO <sub>3</sub>	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>
Na <sub>2</sub> SO <sub>3</sub> + air	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> + air	air	Na <sub>2</sub> SO <sub>3</sub>	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>
Na <sub>2</sub> SO <sub>3</sub> + O <sub>2</sub>	Fe(OH) <sub>2</sub> + O <sub>2</sub>	O <sub>2</sub>	Na <sub>2</sub> SO <sub>3</sub>	Fe(OH) <sub>2</sub>
Na <sub>2</sub> SO <sub>3</sub> + O <sub>2</sub>	Co(OH) <sub>2</sub> + O <sub>2</sub>	O <sub>2</sub>	Na <sub>2</sub> SO <sub>3</sub>	Co(OH) <sub>2</sub>
Na <sub>2</sub> SO <sub>3</sub> + O <sub>2</sub>	Ni(OH) <sub>2</sub> + O <sub>2</sub>	O <sub>2</sub>	Na <sub>2</sub> SO <sub>3</sub>	Ni(OH) <sub>2</sub>
Na <sub>2</sub> SO <sub>3</sub> + O <sub>2</sub>	Cu <sub>2</sub> + O <sub>2</sub>	O <sub>2</sub>	Na <sub>2</sub> SO <sub>3</sub>	Cu <sub>2</sub> O
H <sub>2</sub> SO <sub>3</sub> + air	FeSO <sub>4</sub> + air	air	H <sub>2</sub> SO <sub>3</sub>	FeSO <sub>4</sub>
H <sub>2</sub> SO <sub>3</sub> + air	SnCl <sub>2</sub> + air	air	H <sub>2</sub> SO <sub>3</sub>	SnCl <sub>2</sub>
Fe(OH) <sub>2</sub> + O <sub>2</sub>	Ni(OH) <sub>2</sub> + O <sub>2</sub>	O <sub>2</sub>	Fe(OH) <sub>2</sub>	Ni(OH) <sub>2</sub>
Co(OH) <sub>2</sub> + O <sub>2</sub>	Ni(OH) <sub>2</sub> + O <sub>2</sub>	O <sub>2</sub>	Co(OH) <sub>2</sub>	Ni(OH) <sub>2</sub>
Mn(OH) <sub>2</sub> + O <sub>2</sub>	Ni(OH) <sub>2</sub> + O <sub>2</sub>	O <sub>2</sub>	Mn(OH) <sub>2</sub>	Ni(OH) <sub>2</sub>
Ce(OH) <sub>3</sub> + O <sub>2</sub>	Ni(OH) <sub>2</sub> + O <sub>2</sub>	O <sub>2</sub>	Ce(OH) <sub>3</sub>	Ni(OH) <sub>2</sub>
Na <sub>2</sub> SO <sub>3</sub> + air	Na <sub>3</sub> AsO <sub>3</sub> + air	air	Na <sub>2</sub> SO <sub>3</sub>	Na <sub>3</sub> AsO <sub>3</sub>
Na <sub>2</sub> SO <sub>3</sub> + air	Mn(OH) <sub>2</sub> + air	air	Na <sub>2</sub> SO <sub>3</sub>	Mn(OH) <sub>2</sub>
	Na <sub>2</sub> SO <sub>3</sub> + air	air	Na <sub>2</sub> SO <sub>3</sub>	Na <sub>2</sub> SO <sub>3</sub>
SnCl <sub>2</sub> + air	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> + air	air	SnCl <sub>2</sub>	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>

most intense anti-oxygenic catalyst is also a most intense pro-oxygenic catalyst. Phosphorus sesquisulfide, P<sub>4</sub>S<sub>3</sub>, which is used in the manufacture of matches because it reacts vigorously with oxygen, is pro-oxygen toward styrol and linseed oil; but the same substance acts as an effective anti-oxygen toward benzaldehyde at a dilution of 1 : 1000. Likewise, hydroquinone or methylamine hydroiodide are very active anti-oxygen agents toward acrolein (1 : 1 million) and are pro-oxygen agents toward styrene.

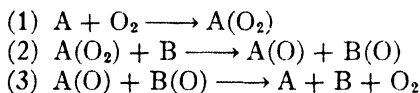
It has been emphasized that negative and inhibiting catalysis occurs most frequently when the catalyst is readily oxidized.<sup>38</sup> For example, the oxidation of sodium sulfite or stannous salts is retarded only by oxidizable substances. The study of the adsorption of oxygen by benzaldehyde, acrolein, acetaldehyde, turpentine and various other substances acting as inhibitors or negative catalysts<sup>93, 94, 95</sup> stresses the fact that all of them are good reducing agents. It has been definitely established that reducing agents such as cane sugar, glucose, and maltose act as negative or inhibiting catalysts in reactions involving auto-oxidation.

Investigations concerning thermal and photochemical reactions led to the belief<sup>40</sup> that they are sensitive to the action of the same inhibitors. A retarding action was found in reactions proceeding in the dark, as well as in the photochemical oxidation of benzaldehyde and sodium sulfite. In some thermal oxidation reactions, inhibitors retard chemical changes by

reacting with the oxygen, causing an oxygen competition which results in a lowering of the velocity of the main reaction.

The retarding action in oxidation processes, known as anti-oxygenic activity, has been established in the production of rubber. When not adequately protected by an antioxidant it is sensitive to oxygen. Antioxidants, such as phenol, pyrocatechol and its derivatives (1 : 100), are introduced into rubber prior to vulcanization. Accelerators used in vulcanizing processes have been characterized as possessing anti-oxygenic properties. Moureu and Dufraisse attributed such anti-oxygenic activity to nitrogenous organic accelerators, for example, aniline, dimethylaniline, *p*-nitrosodimethylaniline, diphenylamine, *p*-phenylenediamine, aminophenols, thiocarbanilid, etc.

The mechanism by which antioxidants act has been described by Moureu and Dufraisse in the following scheme:



The peroxide  $A(O_2)$  of the auto-oxidizable substance oxidizes the anti-oxygen  $B$  with the formation of a peroxide  $B(O)$ , while it itself is converted into another peroxide  $A(O)$ . The two peroxides  $A(O)$  and  $B(O)$  react with each other, regenerating thereby all three initial components, namely,  $A$ ,  $B$  and  $O_2$ . This mechanism indicates that the primary peroxide contains wholly activated oxygen (indicated by parentheses) able to decompose under the influence of the catalyst with liberation of all its oxygen.

Experimental evidence confirming the postulated mechanism has been sought in the influence of light in the presence of a fluorescent substance, such as chlorophyll, upon amines.<sup>52</sup> Certain amines were able to fix molecules of free oxygen, with the formation of an addition compound in which the oxygen is in an active state. When manganese dioxide catalyst was added to this oxygen in the dark, it liberated oxygen in a free state. If  $A$  is the amine and  $B$  the manganese dioxide catalyst then it is apparent that the above mechanism of Moureu and Dufraisse is applicable.

The action of antioxidants was described also as a selective deactivation of active molecules.<sup>110</sup> The velocity of a reaction with an antioxidant participating in it is determined chiefly by the concentration of active molecules. This is assumed to be a function dependent on thermodynamic and statistical laws and not modified by the presence of minute amounts of the catalyst. Moureu and Dufraisse considered it impossible that the remarkable slowing down effected by small amounts of an anti-oxygen in an auto-oxidation process should produce a simple direct or indirect deactivation of activated molecules of oxygen. Perrin<sup>110</sup> opposed the theory of Moureu and Dufraisse<sup>96</sup> by stating that it lacks agreement with the principles of thermodynamics because it assumes that the antioxidant  $B$  catalyzes the destruction of the active peroxide  $A(O_2)$  reverting it to its initial state  $A + O_2$  without catalyzing the reverse reaction, the formation of the peroxide. It is thermodynamically impossible for a catalyst to displace a chemical equilibrium or accelerate a reaction in only one

direction. But it was maintained that if the introduction of a substance small in amount as compared with the reactants modifies the equilibrium, then the equilibrium must be between ordinary and metastable active molecules. The concentration of these molecules is less than that of others and comparable to that of the added substance. This viewpoint, stressed by Dubrissay,<sup>46</sup> Moureu and Dufraisse considered as meeting all the objections to their theory from the viewpoint of thermodynamics.

It is interesting to note that antioxidants do not always function in the same manner;<sup>97</sup> sometimes they possess a protective action toward oxygen and sometimes they have no such effect. While the conversion of acetaldehyde into paraldehyde is not inhibited by antioxidants, the polymerization of trichloroacetaldehyde (chloral) into metachloral is inhibited. On the other hand, the polymerization of phenylacetaldehyde is not inhibited by antioxidants. Furfural is inhibited in its darkening action by the addition of small amounts of hydroquinone, oxygen being one of the factors responsible for discoloration. Chevreul established the fact that no drying of linseed oil takes place in a vacuum and that what causes it to dry is the oxygen adsorbed by the oil when exposed to air. The fixation of atmospheric oxygen may be inhibited by adding an antioxidant to the oil. The condensation of turpentine, which is prevented by the presence of an antioxidant, is also activated by oxygen. Hydroquinone prevents some of the reactions of styrene, such as its conversion into its isomer, metastyrene. Similar results are obtained with diphenylethylene or furfurylethylene.

Inhibiting action is often characteristic not only of one compound, but of whole classes of organic compounds. It has been found<sup>93</sup> that phenols, for example, as a class exhibit an inhibitory power in a number of auto-oxidation processes. The inhibitory power was related to the formation of compounds between the inhibitor and the auto-oxidant and was found to increase with the increase in the number of hydroxyl groups present in the ring structure. This parallels the ease of formation of phenolic polymolecular compounds. A regularity in the relationship between the inhibitory power and compound formation was disclosed by results obtained by different investigators<sup>70, 125</sup> and summarized in a rule<sup>132</sup>

Table 2. (Taylor).

Inhibitor	Substances which Form Condensation Products with Benzaldehyde
Phenol.	Phenol.
Salicylic aldehyde and salicylic acid.	Salicylic acid.
Resorcinol.	Resorcinol.
Hydroquinone.	Hydroquinone.
Guaiacol.	Guaiacol.
$\alpha$ - and $\beta$ -Naphthol.	2,3-Naphthalenediol.
<i>o</i> -Aminophenol.	Ethyl-1,3-dihydroxy-2-naphtholate.
<i>o</i> -Nitrophenol.	$\alpha$ -Nitrotoluene.
Trihydroxy benzene.	Iso-amylamine.
Gallic acid.	Glycerol.
Tannic acid.	<i>p</i> -Amino-oxanilic acid.
	Cyclic ketone base.
	Cyclopentanone.
	Acetonaphthone.

for various acids. A series of acids, such as trichloroacetic, monochloroacetic and acetic, in their respective order, showed a decreasing tendency to compound formation with benzaldehyde in as low a concentration as  $M/1000$ , this decrease running parallel to the decrease in the inhibitory power. The extent of compound formation was found to be dependent upon the strength of the acid.

The parallelism between the inhibitory power and the compound formation may be seen from Table 2 in which are listed inhibitors for the auto-oxidation of benzaldehyde and substances which form condensation products with benzaldehyde.

In Tables 3 to 11 inclusive are shown examples of inhibitors: for catalytic synthetic reactions, Table 3; for catalytic oxidation reactions, Tables 4, 5 and 6; for catalytic decomposition reactions, Tables 7 and 8; for various catalytic reactions, Tables 9, 10 and 11.

Table 3. Inhibitors—Catalytic Synthesis.

Reaction	Inhibitor	Observer
H <sub>2</sub> and O <sub>2</sub> combined catalytically in the presence of clean Pt voltameter electrodes.	Various substances, such as CO and tap grease.	Faraday.
Union of H <sub>2</sub> and O <sub>2</sub> with Pt catalyst.	CO, NH <sub>3</sub> , H <sub>2</sub> S, HCl, CS <sub>2</sub> act anti-catalytically.	Turner, Henry and Faraday.
Union of H <sub>2</sub> and O <sub>2</sub> .	Retarded by H <sub>2</sub> S <sub>2</sub> .	
H <sub>2</sub> and O <sub>2</sub> combined when catalyzed by NO <sub>2</sub> (the reaction proceeding in the dark at 357° has an induction period of about 200 sec.).	About 0.2 mm. of CH <sub>4</sub> is sufficient to prevent the reaction completely.	Foord and Norrish. <sup>18a</sup>
Union of SO <sub>2</sub> with Cl in the presence of camphor probably due to the residual valence of its O <sub>2</sub> ; organic compounds containing =CO, -CO <sub>2</sub> H, or -O- group act as positive catalysts.	Reaction inhibited by organic compounds containing -NO <sub>2</sub> or -SO <sub>2</sub> H group, or a halogen.	Cusmano. <sup>19</sup>
H <sub>2</sub> and Cl <sub>2</sub> combined photochemically; also in other halogen reactions.	O <sub>2</sub> , negative catalyst; probability O <sub>2</sub> combining with a reducing agent under the influence of light.	Dhar. <sup>41</sup> Kistiakowsky
Formation of HCl.	Retarded by O <sub>2</sub> .	Green, S. J. <sup>47</sup>
Photochemical synthesis between hydrogen and chlorine.	Extremely small amount of oxygen.	Lind. <sup>79</sup> Kornfeld. <sup>72a</sup>
Synthesis of CO and O <sub>2</sub> with quartz glass.	Retarded by CO.	Bodenstein and Ohlman. <sup>16</sup>
Synthesis of NH <sub>3</sub> ; (1) T. 500°; (2) temperature even below 400°.	Catalysts must be prepared completely dehydrated since traces of water inhibit formation of ammonia, <i>e.g.</i> , catalysts are prepared by interaction of AlCl <sub>3</sub> with K <sub>4</sub> Fe(CN) <sub>6</sub> (with incomplete washing to preserve the alkali content); (1) ordinary ammonia catalyst; (2) the above type of catalyst.	Uhde; <sup>138a</sup> refer also to Larson and Tour. <sup>77a</sup>
Synthesis of aromatic aldehydes (Gattermann's reaction) (in the preparation of 4-oxy- $\alpha$ -naphthaldehyde after 5 hrs. only $\alpha$ -naphthol was obtained; and only on adding KCl (0.33 mol) did the reaction take place).	Pure Zn cyanide. KCl (0.33 mol) Zn(CN) <sub>2</sub> usually applied contains as impurity alkali chlorides which act catalytically.	Arnold and Sprung. <sup>48</sup>

Table 4. Inhibitors—Catalytic Oxidation.

Reaction	Inhibitor	Observer
Oxidation.	Hydrides of S, Se, Te, P, As and Sb inhibit action of Pt; inhibiting effect probably due to film formation of S, Se, etc., on Pt.	Schönbein. <sup>127</sup>
Oxidation processes in living tissues by free O <sub>2</sub> .	Inhibiting effect due to small amounts HCN.	Bernard. <sup>12</sup>

Table 4 (Continued)

Reaction	Inhibitor	Observer
Oxidation of P in air.	Retarded by H <sub>2</sub> O.	Van der Stadt. <sup>140</sup>
Oxidation of sulfite solutions.	Retarded by primary, secondary and isobutyl alcohols.	Bigelow. <sup>13</sup>
Oxidation of P by O <sub>2</sub> .	Retarded by vapors of various organic substances such as ether, alcohol and turpentine.	Dhar. <sup>37</sup> Kassel. <sup>13a</sup>
Oxidation of SO <sub>2</sub> by O <sub>2</sub> and Pt catalyst.	SO <sub>3</sub> .	Bodenstein. <sup>14</sup>
Oxidation of Na <sub>2</sub> SO <sub>3</sub> .	Mannite and Sn salts; decrease in reaction velocity proportional to the concentration of mannite (d) present.	Bigelow and Titoff. <sup>134</sup>
Na <sub>2</sub> HAsO <sub>3</sub> solution not oxidized by atmospheric oxygen under ordinary conditions; Na <sub>2</sub> SO <sub>3</sub> solution readily oxidized to Na <sub>2</sub> SO <sub>4</sub> by air; when mixed and exposed to air, both oxidations occur simultaneously; oxidation velocity of Na <sub>2</sub> SO <sub>3</sub> is slowed down.	Na <sub>2</sub> HAsO <sub>3</sub> acts as a powerful negative catalyst in the oxidation of Na <sub>2</sub> SO <sub>3</sub> .	Dhar. <sup>37</sup>
Oxidation of NaAsO <sub>2</sub> with KClO <sub>3</sub> (autocatalytic reaction) doubling of the KClO <sub>3</sub> concentration accelerates the reaction considerably more than doubling of the H <sub>2</sub> SO <sub>4</sub> concentration; increase of NaAsO <sub>2</sub> conc. leads to a great decrease in the reaction velocity; the inhibition effect is interpreted in the sense of reduction of OsO <sub>4</sub> to OsO <sub>3</sub> resp., a complex compound formation such as Na <sub>2</sub> [OsO <sub>3</sub> (AsO <sub>2</sub> ) <sub>2</sub> ]; OsO <sub>4</sub> used as catalyst (the reaction velocity about proportional to the catalyst concentration).	Na <sub>2</sub> HAsO <sub>4</sub> .	Sanko and Stefanowski. <sup>125a</sup>
Oxidation of dilute solutions of Na <sub>2</sub> SO <sub>3</sub> .	Inhibiting effect due to benzyl alcohol, manitol (d), and certain phenols.	Titoff. <sup>134</sup>
Oxidation of Na <sub>2</sub> SO <sub>3</sub> by atmospheric O <sub>2</sub> .	Quinol and, to a lesser degree, organic acids such as benzoic, oxalic and salicylic and their salts.	Maxted. <sup>88</sup>
Oxidation of sulfite, using Cu as a catalyst: Cu <sup>2+</sup> ions have the strongest catalytic action.	Arsenite; the rate of oxidation of a mixture of sulfite and arsenite is very small as compared to that of sulfite alone; it is assumed that Cu forms complexes with the arsenite.	Jorissen. <sup>66, 143</sup>
Oxidation of Fe(OH) <sub>2</sub> , Ce <sub>2</sub> O <sub>3</sub> · 6H <sub>2</sub> O and Na <sub>2</sub> SO <sub>3</sub> .	Greatly retarded by presence of carbohydrates, fats, and nitrogenous substances.	Dhar. <sup>37</sup>
Oxidation of ferro ions in weak H <sub>2</sub> SO <sub>4</sub> solution.	Cryogenin, phenylhydrazine, aminophenols decrease the reaction velocity to one-half.	Boutaric and Gautier. <sup>13a</sup>
Oxidation velocities of mixtures of SnCl <sub>2</sub> and Na <sub>2</sub> SO <sub>3</sub> in NaOH solution are less than those of either alone, except when the concentration of stannous chloride is low.	SnCl <sub>2</sub> .	Mujamoto. <sup>89</sup>
Oxidation of Sn salts in air.	Retarded by ferrous salts.	Dhar and Mittra. <sup>38</sup>
Oxidation of I <sup>-</sup> with ClO <sub>3</sub> <sup>-</sup> in aqueous solution over VOSO <sub>4</sub> catalyst; only in the presence of an excess of KI and HCl does the reaction proceed according to the equation: KClO <sub>3</sub> + 6KI + 3H <sub>2</sub> O = 6KCl + 6KOH + 6I <sub>2</sub> . In the ideal case, the reaction follows the kinetic equation: $d(I)/dt = K(KI) \cdot (KClO_3/s)$ . Constant K contains the concentration of the acid and of the catalyst; the temperature coefficient for 10° is 2.87 (T. 25–35°); the inhibition of the reaction is found to be a function of the concentration of this salt.	Phenol and <i>p</i> -nitrophenol active in other reactions are inactive here; hydroquinone and resorcin both greatly retard the I <sub>2</sub> precipitation; by using hydroquinone, quinhydrone is precipitated; obviously the influence of resorcin and hydroquinone is based on self use of chlorate; true inhibitory action is observed in the case of MnSO <sub>4</sub> and of NiSO <sub>4</sub> .	Weber, Liszt and Balzer. <sup>144a</sup>

Table 5. Inhibitors—Catalytic Oxidation.

Reaction	Inhibitor	Observer
Combustion of CO on quartz catalyst.	H <sub>2</sub> O.	Bradford. <sup>20</sup>
Combustion of CO with oxides of Ni and Cu, porcelain and bricks as catalyst.	H <sub>2</sub> O molecules adsorbed do not decrease the reaction; the explanation given by Bradford is to the effect that combustion proceeds in the absence of water vapor partially as dry oxidation.	Bone <sup>18</sup>
Combustion of CO with Au catalyst; water vapor acts as an accelerator; when Ag is used as a catalyst the reaction is retarded.	Water vapor.	Bradford. <sup>21</sup>
Oxidation of unsaturated organic compounds with metal catalysts.	Moisture.	Fokin. <sup>18b</sup>
Oxidation of formic and phosphoric acids by chromic acid.	Mn (ous) salts act as powerful negative catalysts; Mn (ous) salts readily converted into Mn (ic).	Dhar. <sup>41</sup>
Oxidation of oxalic acid by HI.	0.001 mole HCN negative catalyst, reaction stopped by 0.002 mole HCN.	Wieland and Fischer. <sup>14a</sup>
Oxidation of salicylic acid.	1% of antipyretic compounds accelerates the reaction, while 5% slows it down.	Boutaric and Gautier. <sup>19a</sup>
Oxidation of C <sub>6</sub> H <sub>5</sub> · CHO.	Retarded by a trace of quinol (hydroquinone).	Moureu and Dufrasse. <sup>93</sup>
Oxidation of CHCl <sub>3</sub> .	Retarded by a small amount of alcohol.	Dhar. <sup>39</sup>
Oxidation of cystine by methylene blue.	Retarded by HCN.	Toda. <sup>135</sup>
Oxidation of organic S compounds in air.	Retarded by (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O.	Delépine. <sup>42</sup>
Various Mg alkyl halides of the Grignard type show slow oxidation by luminosity on exposure to air.	Retarded by (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O.	Lifschitz and Kalberer. <sup>78</sup>
Oxidation of phenols by H <sub>2</sub> O <sub>2</sub> over FeCl <sub>3</sub> catalyst.	The reaction is retarded by mineral acids and still more by organic acids: acetic, oxalic and citric.	Colin and Senechal. <sup>34a</sup>
Oxidation of phenolphthalein by H <sub>2</sub> O <sub>2</sub> over Cu salts.	Mn salts.	Thomas and Kalman. <sup>133a</sup>

Table 6. Inhibitors—Catalytic Oxidation.

Reaction	Inhibitor	Observer
Oxidation of oils.	Basic unsaturated compounds, such as amines and aromatic phenols and basic inorganic reducing agents most effective inhibiting substances.	Smith and Wood. <sup>129</sup>
Oxidation of various fatty oils: (1) linseed oil;	Strong antioxidants for linseed oil are pyrocatechin, hydroquinone, pyrogallol, <i>o</i> -nitrophenol, $\alpha$ -naphthol, $\alpha$ - and $\beta$ -naphthylamine, eugenol and thymol;	Nakamura. <sup>102</sup>
(2) tsubaki oil;	<i>p</i> -Nitro-aniline is an antioxidant;	
(3) soja oil.	<i>p</i> -Nitro-aniline is a pro-oxidant. The inversion of the oxidizing-acting catalyst depends on the nature of the oil used.	
Photo-oxidation of olive oil, cottonseed oil, corn oil, soja oil, linseed oil, perilla oil, tsubaki oil for which 0.5 per cent <i>p</i> -nitro-aniline is a catalyst; (the pro-oxygen action increases with the iodine number).	Nitro-aniline converts gradually into an anti-oxygen for oils with an iodine number below 120; the conversion into anti-oxygen occurs more rapidly the lower the iodine number.	Nakamura. <sup>103</sup>



Table 6 (Continued).

Reaction	Inhibitor	Observer
Oxidation of cracking benzene.	Anti-oxygen action of 0.01% of coal-tar oil (fraction b. p. 250–275°); the alkali extraction of the corresponding fractions shows the same effect.	Universal Oil Products Co. (Morrell and Dryer). <sup>139a</sup>
Oxidation of benzene.	Leucoquinizarin, leucopurpurin, alizarin and leucopolyoxyanthraquinone; these anti-oxidation agents are added dissolved primarily in benzene and then in benzine (the leucoanthraquinone compounds must contain free OH groups but not in the position 9 and 10 or on the C atoms carrying the quinone groups).	Orelup. <sup>101a</sup>
Oxidation of benzenes or kerosenes (the anti-oxidation agents prevent decolorizing and resin precipitation).	Anti-oxidation action of small amounts of aminophenones, such as 2-amino-5-oxybenzophenone.	Texaco Development Corp. (Story). <sup>132a</sup>
Oxidation of benzenes and prevention of resin formation.	Anti-oxidation action of 0.001–0.1% cresol.	Canadian Industries, Ltd. (Calcott and Lee). <sup>23a</sup>
Oxidation of benzenes and prevention of decoloration.	Aromatic oxy- or amino acids, such as salicylic acid, anthranilic acid, protocatechuic acid and gallic acid or the corresponding acids of the naphthalene or anthracene series.	Standard Oil Development Co. <sup>130'</sup>
Oxidation of petroleum hydrocarbons.	Anti-oxygenic action of small amounts of aliphatic polyamines of the composition $H_2N-CH(R)-CH(R_1)-NH_2$ , where R and R <sub>1</sub> are alkyl groups or their derivatives.	Standard Oil Co. (Voorhees). <sup>130''</sup>
Oxidation of adrenalin.	(1) Metal cations: $Cu^{++}$ , $Fe^{+++}$ , $Mn^{++}$ , $Co^{++}$ ; (2) Amino bodies: glycochol, guanidine carbonate, synthaline B, phenyl urea, phenyl alanine; (3) Phenols and enols: hydroquinone, menthol, ascorbinic acid; (4) Narcotics: barbituric acid, veronal, acetone, chloroform; (5) Sulfohydriis: thiglycolic acid, thiolactic acid, thiourea, cystein, chlorhydrate, l-cystin; (6) $Na_2SO_4$ . Most of the inhibitors are active already in a very high dilution (1:10 <sup>6</sup> ); in the case of metal salts when larger amounts of inhibitor are applied the inhibition is superimposed on catalysis; in general the action of inhibitors is relatively stronger for small amounts of them than for large.	Baur and Obrecht: <i>Z. physik. Chem. (B)</i> , <b>41</b> , 167–78 (1938); refer also to Baur: C. 1930 I 943.

Table 7. Inhibitors—Catalytic Decomposition.

Reaction	Inhibitor	Observer
Decomposition of $NH_3$ into N and H.	Retarded by presence of small amount $H_2O$ .	Than. <sup>133</sup>
Photoelectric decomposition of $NH_3$ .	Platinized glass flask gives smaller yield than non-platinized vessel; small amount of Ra emanation (admixed to $NH_3$ ) (about 15 cm. Hg. decreases the yield (in a flask 5 cm. diameter) up to 60 per cent).	Luyck. <sup>83</sup>
Decomposition of alkaline $H_2O_2$ using $Pb(OH)_2$ as a catalyst.	Rate of decomposition retarded by $Mg(OH)_2$ , $Cd(OH)_2$ , $Ni(OH)_2$ .	von Halbau. <sup>141</sup>

Table 7 (Continued).

Reaction	Inhibitor	Observer
Decomposition of $\text{H}_2\text{O}_2$ in aqueous solution with smooth and little active platinated Pt.	Ultraviolet radiation slows down catalysis.	Pissarjewski. <sup>111</sup>
Photochemical decomposition of $\text{H}_2\text{O}_2$ ; the reaction is believed to proceed according to the equation: $\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}\cdot$ , whereby the recombination of OH radicals plays the essential part and the chain is broken.	Acetone, methylethylketone and diethylketone.	Dain and Schwarz. <sup>112</sup>
Decomposition of $\text{MgO}_2$ (prepared from $\text{Mg}(\text{OH})_2$ and 30% $\text{H}_2\text{O}_2$ ).	Luminal, urotropin, caffen, citronic acid, anthracene and brucine (added in an amount of 0.02).	Katz. <sup>113</sup>
Decomposition of chromic acid in $\text{H}_2\text{SO}_4$ (almost 100%); two superimposed reactions: (1) pseudomonomolecular reaction predominating in 100% acid; (2) bimolecular reaction, occurs in 81% solution.	A colorless reaction product, precipitating on heating, is responsible for the slowing down of the reaction (in dilute solutions the reaction products have a positive catalytic influence).	Snethlage. <sup>110''</sup>

Table 8. Inhibitors—Catalytic Decomposition.

Reaction	Inhibitor	Observer
Decomposition of CO, using Ni as a catalyst.	Catalytic activity of Ni, when alloyed with 50% Sn, practically destroyed; suitable Ni-Ni spacings in alloyed catalyst infrequent.	Tropsch and von Philippovich. <sup>117</sup>
Decomposition of $\text{Ca}(\text{HCO}_3)_2$ over coke, active charcoal, graphite; $\text{CaCO}_3$ catalysts.	Zn splinter, solution of Zn salt, Cu and Th salts.	Stumper. <sup>131a</sup>
Decomposition of isopropyl alcohol on bauxite (unimolecular reaction).	Retarded by $\text{H}_2\text{O}$ .	Dohse and Kälberer. <sup>118</sup>
Decomposition of oxalic acid in $\text{H}_2\text{SO}_4$ solution.	$\text{H}_2\text{O}$ .	Bredig and Lichty. <sup>119</sup>
Decomposition of oxalic acid by strong $\text{H}_2\text{SO}_4$ .	Retarded by presence of small amount $\text{H}_2\text{O}$ .	Than. <sup>123</sup>
Decomposition of triethyl sulfonium bromide in acetone and to a lesser extent in acetic acid solutions.	$\text{H}_2\text{O}$ .	von Halbau. <sup>141</sup>
Decomposition of diazo esters in alcoholic acid solution.	Rate of decomposition slowed down by presence of $\text{H}_2\text{O}$ .	Bredig and Fränkel. <sup>124</sup>
Decomposition of diazo acetic acid ester in an alcoholic solution.	Water.	Millar. <sup>91a</sup> Braune. <sup>21a</sup>
Decomposition of solutions of organic ferric salts and tetrabenzoyl ethylene.	Retardation effect of oxygen due to oxygen combining with the reducing agent.	Dhar. <sup>41</sup>
Decomposition of diethyl ether catalyzed by NO (498-607°) in a quartz vessel.	While large amounts of NO accelerate the reaction, small amounts of NO (0.5 mm.) decrease the reaction velocity to about one-half; maximum of the inhibiting action for about 2 mm.; the reaction velocity drops to about $\frac{1}{4}$ to $\frac{1}{4}$ of the normal velocity.	Staveley and Hinshelwood. <sup>130a</sup>
Decomposition of dimethyl ether.	NO.	Thompson and Meissner. <sup>122b</sup>
(1) Thermal decomposition of propionaldehyde. (2) Thermal decomposition of acetaldehyde.	Small amounts of NO (few mm. Hg) inhibit the reaction (1); no influence of NO upon the reaction (2).	Staveley and Hinshelwood. <sup>130a</sup>
Decomposition of acetaldehyde induced through ethylene oxide.	Slowed down by helium acetone, methanol and NO; NO action is the strongest.	Fletcher and Rollefson. <sup>49''</sup>

Table 8 (Continued).

Reaction	Inhibitor	Observer
Decomposition of ethane, acetaldehyde, propionaldehyde and butyraldehyde; T. 600°; ethane decomposition, average chain length 21, pressure 50 mm.; ethane decomposition, average chain length 6, pressure 500 mm.; acetaldehyde decomposition, average chain length 1, pressure 500 mm.; propionaldehyde decomposition, intermediate between the above values; butyraldehyde decomposition, chain length slightly greater than that of propionaldehyde. The decomposition of simple organic compounds may follow either through a direct conversion into stable products or over free radicals originating on splitting, and these radicals induce the procedure of the reaction through reaction chains. The results of this investigation favor the second possibility.	NO.	Staveley and Hinshelwood. <sup>130a</sup>
Decomposition of ethane to $C_2H_4$ and $H_2$ ; T. 612°; pressure 1-8 mm.	Propene added to ethylene decreases the decomposition rate.	Dintzes, Kvyatkovskii and Frost. <sup>45a</sup>
Decomposition of ethane; the simple Rice-Hertzfeld free radical or chain mechanism assumed inadequate explanation for the reaction; the ethyl group is not the intermediate product in the decomposition of ethane (Rice).	Retarding effect of the unsaturated products of the reaction: $C_2H_4 + H \rightarrow C_2H_5$ . Propene has the retarding effect on the decomposition of ethane.	Frost. <sup>51a</sup> Frost. <sup>51b</sup>

Table 9. Inhibitors—Various Catalytic Reactions.

Reaction	Inhibitor	Observer
Manufacture of $H_2SO_4$ by atmospheric oxidation of $SO_2$ using Pt as catalyst.	Rapid loss of Pt activity; retarded by presence of minute amount As compounds; purified gases free from dust must be used.	Phillips (Patent, 1831).
Deacon Process for manufacture Cl used in Le Blanc Soda Process—CuCl as catalyst.	By-products Le Blanc Process, HCl and $H_2SO_4$ , the latter inhibiting the reaction or poisoning the CuCl catalyst; a method for purification of HCl gas suggested.	Hasenclever, 1883.
Chlorination reaction; chain mechanism postulated: (1) $Cl_2 \rightleftharpoons 2Cl$ (2) $RH + Cl \rightarrow R + HCl$ (3) $R + Cl_2 \rightarrow RCl + Cl$ the catalyst initiates chains by producing chlorine atoms or free organic radicals.	Free oxygen.	Pease and Walz. <sup>109a</sup>
One part $H_2O_2$ diluted in 200 million parts $H_2O$ effects change in color of $Cu(OH)_2$ .	Retarded by small amounts of Mg salts and other electrolytes.	Quartaroli. <sup>112</sup>
Changes in the coloration of freshly precipitated $Cu(OH)_2$ in the presence of $H_2O_2$ in two steps: (1) darkening up to black, and (2) following contraction.	Traces of Mg, Ni and Co.	Quartaroli. <sup>113</sup>
Reduction of NiO.	$H_2O$ .	Sabatier and Espil. <sup>122a</sup>
Dissolution of metals in $HNO_3$ .	Retarded by reducing agents excepting formic acid.	Palit and Dhar. <sup>100</sup>
Reaction between $KMnO_4$ and $H_2O_2$ , whereby Mn ions are very active catalysts for small concentration $H_2O_2 = 0.005$ (maximum reaction velocity); $H_2O_2 = 0.2$ (minimum reaction velocity).	Inhibition for the high conc. $H_2O_2$ reaction is caused by stirring.	Bailey and Taylor. <sup>7a</sup>
The reaction: $2H_2SO_4 + 2H = H_2S_2O_8 + 2H_2$ yield of $2n$ $H_2SO_4$ by oxidation is strongly decreased by $10^{-3}$ mol/liter HCl.	$1.0 \cdot 10^{-3}$ mol/liter HCl; $2.10 \cdot 10^{-2}$ mol/liter HCl decreases the anode potential drop of the $2n$ $H_2SO_4$ by 23 volts and the cathode potential drop is increased by 12 volts; HF has no influence; K salt increases the yield.	Klemenc and Kalisch. <sup>71a</sup>

Table 10. Inhibitors—Various Catalytic Reactions.

Reaction	Inhibitor	Observer
Chlorination of $\text{CHCl}_3$ without the use of a catalyst.	Retarded by $\text{FeCl}_3$ ; a case of negative catalysis.	Gault and Trauffault. <sup>64</sup>
Dehydration of alcohol at 250° with alumina containing various other substances.	Retarded by $\text{CaO}$ , $\text{H}_3\text{PO}_4$ , $\text{Co}_2\text{O}_3$ , $\text{CuO}$ and $\text{Cu}_2\text{O}$ , $\text{WO}_3$ , $\text{H}_2\text{SO}_4$ and $\text{Hg}$ in the order given.	Charrion. <sup>20</sup>
Hydrogenation with Pt and Pd catalysts.	Ni, Co, Fe, Cu.	Paal and Windisch. <sup>108</sup>
Hydrogenation reaction.	Alkali.	Foresti and Chiammo. <sup>69a</sup>
Reduction of benzaldehyde.	Retarded by pure Pt.	Adams and Carothers. <sup>1</sup>
Reaction between hydrogen and sodium picrate using Pd as a catalyst.	CO retards catalytic action of Pd; Pd when treated with CO loses its power to occlude $\text{H}_2$ at any rate at low temperature.	Paal and Hartmann. <sup>107</sup> de Hemptinne. <sup>61</sup>
Reaction between bromo-substituted aliphatic acids and $\text{AgNO}_3$ in an alcoholic solution.	$\text{HNO}_3$ exerts an anticatalytic action.	Seuter and Porter. <sup>128</sup>
Conversion of acetophenoneoxime to acetanilide in conc. $\text{H}_2\text{SO}_4$ .	Water.	Lobry de Bruyn and Sluiter. <sup>80</sup>
Diazotation of aniline by Cl ions; the same reaction catalyzed by Br ions renders a reaction velocity 100 times greater than that for Cl ion catalysis because the slowing down action of H ions is almost eliminated.	H ions.	Schmidt and Schubert. <sup>125a</sup> Schmidt and Schubert (Refer to C. 1937 I 3301).
Explosion reactions in $\text{CH}_4$ -air mixtures.	Isobutyl chloride, propyl bromide, ethyl iodide (depending upon concentration, the explosion may be hindered or promoted); thus the whole explosion interval has to be studied to estimate the inhibition action; sulfuryl chloride causes the lowering of the upper and the increase of the lower explosion limit of $\text{CH}_4$ -air mixtures and therefore cannot make non-explosive mixture into explosive; with 6.4% $\text{SO}_2\text{Cl}_2$ the $\text{CH}_4$ -air mixtures cannot be brought any more to explosion; similar action has the content of 5.5% $\text{SiCl}_4$ , 1% $\text{CCl}_4$ inhibits explosion completely.	Jorissen. <sup>67a</sup>
Explosion reactions in CO-air mixtures.		
Polymerization of benzene pretreated according to Gray's method; the mixture of a polymerization benzene and straight-run benzene possesses a susceptibility equal to that of ordinary cracking benzene.	Small amounts of ordinarily used inhibitors cause the same favorable action as in the case of cracking benzene.	Ross and Henderson: <i>Refiner &amp; Natural Gasoline Mfr.</i> , <b>18</b> , 140-43. Ross and Henderson: <i>Oil and Gas J.</i> , <b>37</b> (No. 45) 107-08 (1939).
Preparation of isooctane from cracking benzene; first propane is removed and the sulfur content is decreased by a two-fold alkali washing, then the butane-butylene fraction is isolated; after further washing with alkali, this fraction is polymerized in a limited temperature interval selectively to octylenes, and finally hydrogenated under diminished pressure; the hydrocarbon mixture obtained has a mix value corresponding to 2,2,4-trimethyl pentane and is mixed as commercial isooctane with straight-run benzene and isopentane to an aviation propellant with an octane number of 100.	Activated Ni.	Coulthurst: <i>Oil and Gas J.</i> , <b>37</b> (No. 50) 50-51 Coulthurst: <i>Refiner and Natural Gasoline Mfr.</i> , <b>18</b> , 134-37 (1939).

Table 10 (Continued).

Reaction	Inhibitor	Observer
Polymerization of butanes from natural gas (Shamrock Oil and Gas Corp.); butane is cracked and catalytically polymerized, whereby two products are obtained: (1) through pyrolysis (in butane cracking oven) forms polymerization product which is about 8-10 per cent of the total polymer production and partly as absorption oil, which is used again by the separation of $\text{CH}_4$ ; (2) the catalytic polymerization product which was formed from olefins in the towers containing the catalyst; these products are suitable for mixing with special motor propellants, have a high octane number, a low sulfur and resin content, and are highly sensitive with respect to inhibitors.		Mack: <i>Oil and Gas J.</i> , 37 (No. 51), 60, 62, 64 (1939).
Polymerization of acrylic acid, its homologs and derivatives; distillation of crude acrylic acid in vacuum in the presence of hydroquinone; 77% of acrylic acid is obtained with 0.8% $\text{SbCl}_5$ ; under ordinary conditions 88% of acrylic acid is obtained.	0.1-1% water-free $\text{SbCl}_5$ , $\text{SbCl}_3$ , $\text{AsCl}_3$ , $\text{AsCl}_5$ , $\text{AlCl}_3$ , or potassium-bismuth iodide.	Imperial Chemical Industries, Ltd. (Crawford): U.S.P. 2,143,941, Jan. 17, 1939.

Table 11. Inhibition Effect through Drying.\*

Reaction	Observer
Reduction of gold salts by $\text{H}_2$ ; salts of Ag and Au adsorbed on a fabric readily attacked by $\text{H}_2\text{S}$ ; oxidation of P or any combination with oxygen in combustion requires water.	Mrs. Fulhame: "Essay on Combustion." (London) 1794; quoted by Thomson in "A System of Chemistry," 2, 454 (1802).
$2\text{HCl} + \text{CaO} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O}$ .	Higgins: "Experiments and Observations on the Atomic Theory," 1814. Veley: <i>J. Chem. Soc. (London)</i> , 63, 821 (1893); 65, 1 (1894). Hughes: <i>Phil. Mag.</i> (1892).
In oxidation processes oxygen vigorously dried is not suitable.	Dixon: <i>Proc. Roy. Soc.</i> 37, 56 (1884).
Oxidation of K, As, Bi, Pb, Zn, W, Fe, Ca by air.	Bonsdorff: <i>Ann. Phys.</i> , 41, 293; 42, 325 (1837).
Ethylene plus chlorine, forming ethylene dichloride.	Regnault: <i>Ann. Chim. Phys.</i> (2), 60, 176 (1838).
Salts of Pb, Hg, Cu plus $\text{H}_2\text{S}$ to form sulfides.	Parnell: B. A. Reports, 51 (1841). Hughes: <i>Phil. Mag.</i> (1893).
Zn, Cu, Fe plus $\text{Cl}_2$ to form chlorides.	Andrews: <i>Trans. Roy. Irish Acad.</i> , 19, 398 (1842).
Zn, Cu, Fe plus $\text{Br}_2$ to form bromides.	
Reactions of oxides of Ca, Ba, Mg, Na and K.	Kolb: <i>Compt. rend.</i> , 64, 861 (1867). Debray: <i>Compt. rend.</i> , 26, 603 (1848). Veley: <i>Ber.</i> , 29, 577 (1895).
Reactions of hydroxides of Ca, Ba, Mg, Na, K with $\text{CO}_2$ to form carbonates.	Baker: <i>J. Chem. Soc.</i> , 661 (1910). Baker: <i>J. Chem. Soc.</i> , 400 (1902). Baker: <i>J. Chem. Soc.</i> , Presidential Address (1928).
$\text{CO} + \text{O}_2$ . $\text{H}_2 + \text{Cl}_2$ . $2\text{H}_2 + \text{O}_2$ .	Baker: <i>J. Chem. Soc.</i> , 646 (1900); <i>J. Chem. Soc.</i> , 91, 1862 (1907).
Dissociation of $\text{PCl}_5$ and $\text{HgCl}_2$ .	Norrisch: <i>J. Chem. Soc.</i> , 123, 3006 (1923); 55, 1926. Davies: <i>J. Am. Chem. Soc.</i> , 50, 2769 (1928). Baker: <i>J. Chem. Soc. (London)</i> , 65, 611 (1894).
$\text{C}_2\text{H}_4 + \text{Cl}_2$ ; $\text{C}_2\text{H}_4 + \text{Br}_2$ .	
$\text{CaO} + \text{SO}_2 \rightarrow \text{CaSO}_4$ . $\text{CuO} + \text{SO}_2 \rightarrow \text{CuSO}_4$ . $\text{CaO} + 2\text{NH}_4\text{Cl} \rightarrow \text{CaCl}_2 + 2\text{NH}_3 + \text{H}_2\text{O}$ .	Baker: <i>J. Chem. Soc.</i> , 65, 611 (1894).
Ammonia and HCl freed from moisture do not form solid $\text{NH}_4\text{Cl}$ and it may be volatilized without decomposition when it is absolutely dry.	

\* These examples are quoted in the literature, but there is rather strong evidence that drying has no marked effect in itself and that inhibition was rather due to some substances of unknown nature.

Table 11 (Continued).

Reaction	Observer
Carbon and phosphorus not combustible in dry oxygen.	Baker: <i>J. Chem. Soc.</i> , <b>47</b> , 349 (1886).
$\text{HCl} + \text{CaCO}_3$ .	Baker: <i>Proc. Roy. Soc. (London)</i> , <b>45</b> , 1 (1889); <i>J. Chem. Soc. (London)</i> , <b>47</b> , 349 (1885).
$\text{H}_2\text{S}$ + metallic salts or oxides.	Cohen: <i>Chem. News</i> , <b>54</b> , 305 (1886).
$2\text{Na} + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2$ .	
$2\text{Al} + 6\text{HCl} \rightarrow 2\text{AlCl}_3 + 3\text{H}_2$ .	
Tungstates, silicates, etc. from solid acids and bases by heating.	Yander and Stamm: <i>Z. anorg. allg. Chem.</i> , <b>190</b> , 65 (1930).
Allotropic conversions of solid $\text{P}_2\text{O}_5$ as well as of solid $\text{SO}_3$ .	A. Smits and Rütgers: <i>J. Chem. Soc. (London)</i> , <b>125</b> , 2573 (1924).
	A. Smits: <i>J. Chem. Soc.</i> , <b>125</b> , 1068 (1924); <i>Z. phys. Chem. (A)</i> , <b>152</b> , 432 (1921).
Conversion of arsenic trioxide into its octahedral isomer (porcelain-like).	Winkler: <i>J. prakt. Chem. (2)</i> , <b>31</b> , 247 (1885).
$2\text{H}_2 + \text{O}_2$ (thermal $\sim 600^\circ$ ).	
$\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ (visible light $\sim 250^\circ$ ).	Bodenstein: <i>Z. phys. Chem. (B)</i> , <b>20</b> , 451 (1933).
$2\text{HCl} \rightarrow \text{H}_2 + \text{Cl}_2$ (ultraviolet light $\sim 250^\circ$ ).	
$\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$ (visible light $\sim 20^\circ$ ).	
$\text{SO}_2 + \text{Cl}_2 \rightarrow \text{SO}_2\text{Cl}_2$ (visible light $\sim 20^\circ$ ).	
$2\text{CO}_2 \rightarrow 2\text{CO} + \text{O}_2$ (ultraviolet light $\sim 250^\circ$ ).	
$2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ (ultraviolet light $\sim 20^\circ$ ).	
The dried gases $\text{NH}_3$ and $\text{CO}_2$ do not react: $2\text{NH}_3 + \text{CO}_2 = \text{CO}(\text{NH}_2)_2\text{ONH}_4$ .	Joshida: <i>Proc. Imp. Acad. (Tokyo)</i> , <b>12</b> , 191-194 (1936).
It is assumed that $\text{H}_2\text{O}$ reacts in the form of a complex $\text{NH}_3 \cdot \text{H}_2\text{O}$ ; the mechanism is:	Joshida: (Refer to London C. 1930 I 1738).
(1) $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 \cdot \text{H}_2\text{O}$	
(2) $\text{NH}_3 \cdot \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{CO} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{NH}_2 \end{smallmatrix} + \text{H}_2\text{O}$	
(3) $\text{CO} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{NH}_2 \end{smallmatrix} + \text{NH}_3 \rightarrow \text{CO} \begin{smallmatrix} \text{ONH}_2 \\ \diagup \\ \text{NH}_2 \end{smallmatrix}$	
The reaction is greatly influenced by inert gases and the walls of the container.	

### Inhibitors in Autocatalytic Reactions

Autocatalytic reactions are a separate class in which one of the reaction products acts catalytically. There exist both positive and negative autocatalytic reactions, as illustrated in Tables 12 and 13. The idea of Moureu and Dufraisse that elements, as well as their respective compounds, show a "relationship of reverse catalysis," that is, can function either as a pro-oxidant or as an antioxidant, has been extended to autocatalytic reactions. The explanation for the variation in the intensity and direction of the reaction was sought in the chemical structure of the agents responsible for the changes. Iron, considered a positive auto-oxidizing agent and therefore pro-oxygenic, has been claimed to have an anti-oxygenic action when used in the colloidal state.<sup>11</sup> In this respect iron is not unique because other elements may also function either as pro-oxidants or antioxidants.<sup>47</sup> The following iron compounds were shown to be antioxidants: iron oxide toward furfural; iron hydroxide toward sodium sulfite in a slightly alkaline solution; ferric chloride toward benzaldehyde and furfural; iron acetyl acetonate toward sodium sulfate and furfural; oxyhemoglobin, carboxyhemoglobin and methamoglobin toward furfural and to a limited extent toward acrolein and sodium sulfite.

Antioxidants are substances easily oxidizable and easily adsorbed.

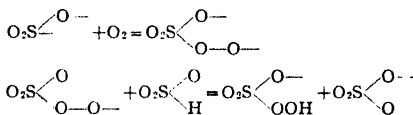
Typical antioxidants are sulfides, iodine, quinol or benzyl alcohol. Atmospheric oxidation of an aldehyde may be prevented by these antioxidants when present in a concentration as low as 0.01 per cent.

Table 12. Positive Autocatalysis.

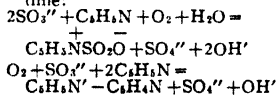
Reaction	Autocatalytic Agent	Observer
Decomposition of thiosulfate by acid.	Free sulfur.	Foussereau. <sup>50</sup>
Decomposition of stibine at 14°.	A deposit of antimony on the walls of the reaction vessel increased the reaction velocity.	Stock and Guttman. <sup>121</sup>
Decomposition of dry arsine in a glass vessel.	A deposit of arsenic on the walls of the reaction vessel increased the reaction velocity.	Cohen. <sup>84</sup>
Hydrolysis of esters in the presence of large amounts of water.	Hydrogen ions of the acid resulting from hydrolysis.	Maxted. <sup>85</sup>
Heat hydrolysis of cane sugar.	Acids produced by inversion of aqueous sugar solutions.	Kullgren. <sup>78</sup>
Slow oxidation of linseed oil (drying oils); driers, compounds of lead or manganese.	A peroxide formed from the oil during oxidation.	Genthe. <sup>86</sup>

Table 13. Inhibition of Positive Autocatalysis.

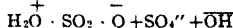
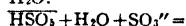
Reaction	Inhibitor	Observer
Auto-oxidation of sodium sulfite in slightly alkaline solution.	Anti-oxidant action of iron hydrate.	Dufraisse and Horclois. <sup>17</sup>
Auto-oxidation of sodium sulfite.	Anti-oxidant action of ferrous ammonium sulfate and iron acetylacetonate; pro-oxidant action of ferric salts.	Dufraisse and Horclois. <sup>17</sup>
Auto-oxidation in the titration of sulfite solutions.	Manitol and glycerin.	Kurtenacker and Wollak. <sup>78</sup>
Photochemical auto-oxidation of Na <sub>2</sub> SO <sub>3</sub> solutions or with Cu catalyst in the dark. Maximum oxidation velocity for pH for which more than half of the sulfite is present as bisulfite.	C <sub>2</sub> H <sub>5</sub> OH; sensitivity against the inhibitor disappears for high bisulfite concentrations; the retarding action of alcohols is connected with an induced reaction in which the bisulfite dehydrogenates losing 2 H atoms; the mechanism suggested on the basis of Haber and Franck's conception is:	Backstrom. <sup>7</sup>



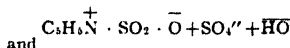
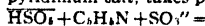
Auto-oxidation of aqueous sulfite solutions in the presence of pyridine:



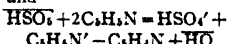
In a strong alkaline solution pyridine acts as an inhibitor, while in an acid sulfite solution pyridine, as a base, acts as an accelerator by decreasing the H<sup>+</sup> concentration and increasing the concentration of the sulfite; the radical HSO<sub>3</sub>· (monothionic acid) which together with O<sub>2</sub> gives HSO<sub>3</sub>·, appears to be a chain carrier and may react with H<sub>2</sub>O:



Pyridine, as the result of more additive character, may enter the reaction more readily than water so that the formation of n-pyridinium sulfuric acid, as well as pyridylpyridinium salt, takes place:



and

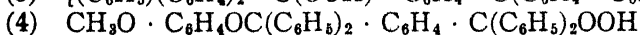
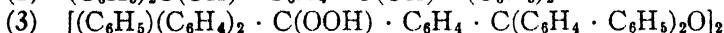
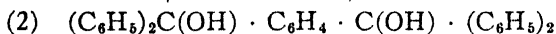
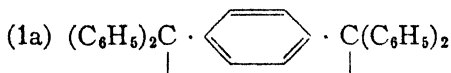
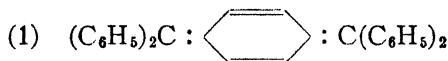


Baumgarten.<sup>106</sup>

Table 13 (Continued).

Reaction	Inhibitor	Observer
Auto-oxidation of sodium bisulfite solution at 20°; pH = 7.0.	Sulfohydryl bodies, such as glutathion (G.SH and G.SSG), cystein, cystin, thilactic acid (complete inhibition; while sugar solution and concentrated KCN solution inhibit markedly).	Ghosh and Rakshit. <sup>11a</sup>
Oxidation of hydroquinone, dioxy-acetone and pyrogallol with O <sub>2</sub> .	The above thiols and disulfides hinder the reaction only when taken in higher concentration.	
Oxidation of cysteins.	Equimolecular amounts of HS glutathion; inactivation of energy-rich oxygen molecules by the thiols is assumed as explanation for the inhibition effect.	
Auto-oxidation of NaO <sub>2</sub> PH <sub>2</sub> starts with the dehydrogenation of the ion; chain mechanism passes through mono-per-phosphoric acid. $\begin{array}{l} \text{H}_2\text{P}'\text{O}_2' \xrightarrow{(\bar{\text{H}})} \text{HP}'\text{O}_2' \\ \text{HPO}_2' + \text{O}_2 \xrightarrow{\quad} \text{HPO}_4' \\ \text{HPO}_4' + \text{H}_2\text{PO}_2' \xrightarrow{\quad} \text{H}_2\text{PO}_4' + \text{HPO}_2' \end{array}$	Small amounts of FeO or Fe <sub>2</sub> O <sub>3</sub> .	Backström. <sup>6</sup>
Auto-oxidation of benzaldehyde and acrolein.	Anti-oxidant action of FeI <sub>2</sub> ; FeCl <sub>3</sub> , a pro-oxidant.	Dufraisse and Horclois. <sup>47</sup>
Auto-oxidation of benzaldehyde.	Anti-oxidant action of colloidal iron.	Berl and Winnacker. <sup>11</sup>
Auto-oxidation of benzaldehyde.	Polyenes, e.g., tetraphenyl ethylene < butadiene < hexatrien < octa-tetraene.	Wittig and Kröhne. <sup>146a</sup>
Auto-oxidation of benzaldehyde.	A few per cent of an aminophenol, e.g., N-methyl-p-amido phenolsulfate, pyramidon, anilin cryogenin, quinine sulfate, antipyrin decrease the effect to 1/3-1/50.	Boutaric and Gautier. <sup>10a</sup>
Auto-oxidation of furfural.	Anti-oxidant action of ferrous oxide, ferric chloride and iron acetyl acetate.	Dufraisse and Horclois. <sup>47</sup>
Auto-oxidation, respectively, of furfural, <acrolein, <sodium sulfite and <benzaldehyde.	Oxyhemoglobin, carboxyhemoglobin, methemoglobin, α-chlorhemin and β-bromhemin.	Dufraisse and Horclois. <sup>47</sup>
Auto-oxidation of furfural.	White phosphorus and phosphoric acid; a gradual slowing down of the oxidation process followed by a complete cessation of the reaction. Red phosphorus acts similar to white phosphorus, but its reaction is less intense.	Moureu, Dufraisse and Badoche. <sup>59</sup>
Auto-oxidation of furfural.	Sodium sulfite; a slowing down of the oxidation process in alkaline solutions and an acceleration in slightly acid solutions.	
Auto-oxidation of cyclohexane.	Pyrex brand glass containing As <sub>2</sub> O <sub>3</sub> or addition of H <sub>2</sub> O.	Stephens. <sup>120a</sup>

Wittig and Kröhne<sup>146a</sup> interpret the auto-oxidation of tetraphenyl-*p*-xylylene according to schemes:





The course is interpreted in the sense that a biradical (1a) binds 1 mol  $O_2$ , which with it free valency further attacks (1a); the compound so formed again adds  $O_2$ , which produces a further bridge to (1a), etc. This reaction apparently stops when the free valence of an  $O_2$  collides with a mobile H atom and converts it into an O.OH group.

The inhibition action of polyenes in auto-oxidation of benzaldehyde is believed to be a function of the number of C:C bonds. In the auto-oxidation the primary step of xylylene peroxide is the dehydrogenation of the hydroquinone monomethyl ether, and the free radical originated thereby is added to another unsaturated C atom of xylylene.

The assumed relationship between anti- and pro-oxidants has been proved in the auto-oxidation of abietic acid,<sup>48</sup> with cobaltous oxide as a catalyst. Either a neutral salt of cobalt abietate or a complex compound of cobalt abietate and abietic acid was formed. A highly adsorptive complex—cobalt abietate-abietic acid—was found present in small amounts by analyzing with the adsorption spectra method, and was held responsible for the anti-oxygenic action. This complex, identified as an intermediate oxide in the oxidation of abietic acid, is formed autocatalytically in the reaction. The actual reversion of pro-oxidant action into the antioxidant action has been demonstrated by the same example involving auto-oxidation of abietic acid with a cobalt oxide catalyst, and hydroquinone as antioxidant.

In autocatalysis the anti-oxygenic action of B is due to its association with the active agent AO to form an inactive combination. In the present case spectroscopic study<sup>48</sup> furnished evidence for an association. Three adsorption bands were obtained (1) from neutral cobalt abietate, a violet-pink band covering a wave length between  $460\mu\mu$ – $570\mu\mu$ ; (2) from oxidized cobalt abietate and abietic acid, a brown-green band; and (3) from a complex compound of cobalt abietate and oxidized abietic acid, a green band, covering wave lengths below  $550\mu\mu$ . The anti-oxygenic action of hydroquinone caused the disappearance of the complementary color band and the appearance of the initial adsorption spectra; the mechanism of its action was thought to destroy the green-colored complex compound by associating itself with the oxidized abietic acid liberating thereby cobalt abietate. Thus the action of negative catalysts and inhibitors was postulated as the formation of inactive complexes, while active complexes (activators stabilizing the normal AO of autocatalysis) manifest themselves in the action of positive catalysts. A certain ratio for the amount of the oxide of the catalyst AO present in the reaction and that of the antioxidant necessary for stopping the oxidation process was established. Complete oxidation at the beginning of the reaction was retarded by 0.1 : 100 hydroquinone for 1 : 100 cobalt compound, but when this process had reached its maximum velocity 1.4–1.6 : 100 hydroquinone was required to check it. The influence exerted by the amount of the catalyst on the velocity of the oxidation was also studied, and it appears that for the upper concentrations down to 0.01 : 100 cobaltous oxide the velocity of oxidation was rapid—corresponding to positive catalysis. For 0.001 : 100 cobaltous oxide the velocity of oxidation was less rapid, namely,

that of negative catalysis. The intermediate concentration corresponding to both positive and negative catalysis was 0.005 : 100 cobaltous oxide. Abietic acid, A is oxidized in two successive stages, namely, AO, and AO<sub>2</sub>, after which the oxidation proceeds slowly. For marked inhibition to occur in catalysis, the rate of the reaction between the inhibitor and the reactant should be rapid as compared with the rate of the reaction itself. Therefore the kinetics of the reactions in negative and inhibiting catalysis must be considered.

It is true that for any autocatalytic reaction proceeding in a liquid phase the velocity of the reaction gradually increases with the increase in the concentration of the catalyst; but when a decrease in the concentration of the reactants counteracts this influence of the concentration of the catalyst, the velocity of the reaction is decreased. Therefore, autocatalytic reactions are graphically expressed by curves of the sine type.<sup>85</sup> The mathematical expression for an autocatalytic reaction obeys two requirements: (1) No catalyst is present at the beginning of the reaction, and (2) the reaction velocity is proportional to the concentration of the reaction product.

The velocity of a monomolecular reaction in which one of the components acts as a retarding agent in negative autocatalysis may be expressed by applying the equation:<sup>106</sup>

$$\frac{dx}{dt} = K_1(a - x) - K_2x(a - x)$$

where  $x$  denotes the quantity of the negative catalyst produced at time  $t$ . Taylor criticized the validity of this equation, assuming that certain values for  $K_1$  and  $K_2$  would change the sign of the value  $\frac{dx}{dt}$  reversing the reaction; such a possibility has not as yet been proved.

Another equation<sup>100</sup> suggested for the liquid phase was as follows:

$$\frac{dx}{dt} = K \frac{(a - x)}{x}$$

in which  $x$  is interpreted as the concentration of the negative catalyst or inhibitor exerting its influence upon the rate of the reaction. On the other hand, the term involving the inhibitor concentration in catalysis has been suggested to be present normally in the denominator.<sup>128</sup> Taylor's<sup>132</sup> expression for the rate of inhibition is in accordance with the Law of Mass Action:

$$(A) = K \left( \frac{AB}{B} \right)$$

in which  $A$  is the concentration of the positive catalyst to be removed by the inhibitor;  $B$  is the concentration of the inhibitor;  $K$  is the constant of the mass action; and  $AB$ , the concentration of the undissociated complex may be regarded as a constant. These are the equations proposed for the velocity determinations whereby the extent of inhibition in catalytic reactions may be checked.

Autocatalytic reactions in solid phase are rare because of the frequent formation of the liquid phase during the reaction. This objection appears to be overcome in the thermal decomposition of oxygen-containing compounds and carbonates in the solid phase. It is also stated<sup>5, 62</sup> that potassium permanganate, without melting, gives only solid or gaseous decomposition products. The catalytic sensitivity of the reaction, as well as its autocatalytic reactivity, has been proved<sup>122</sup> and interpreted by the equations:

$$x_t^{1/3} - x_{t_0}^{1/3} = 1/3K_1(t - t_0), \quad \text{or} \\ \frac{x_t^{1/3} - x_{t_0}^{1/3}}{t - t_0} = K$$

where  $x$  denotes the amount of the decomposition product, while  $t - t_0$  corresponds to the time required for its formation. This equation was applied and found to hold true for the interval of increase in the reaction velocity up to a certain maximum. The autocatalytic reaction in a solid phase is considered to consist<sup>122</sup> of two independent processes: (1) the formation of nuclei of the autocatalyst at single points on the lattice surface, and (2) the spreading of the reaction around these centers. The zones of the decomposition products cross, filling out gradually the crystal surface before the maximum of the reaction velocity is attained. A difference which is observed in the shape of the velocity curves for powdered and non-powdered solid material is ascribed to the difference in the number of initial points of growth or nuclei. The interval of the ascendance of the curve before reaching a maximum is greater the longer the zones grow, and the zone length in turn is a function of the size of the nuclei, or their number.

Thus, the actual mechanism of autocatalysis in solid phase is believed<sup>122</sup> to be as follows: nuclei of the autocatalyst originate at the surface; as the reaction proceeds, a spreading from the surface into the interior takes place, the total surface becoming covered by the autocatalyst. A similarity between autocatalysis in solid phase proceeding from single centers and boundary reactions called "topochemical reactions"<sup>73</sup> is evident in that they both comply with the same formula or show like kinetics. However, two different factors are responsible for the course of the reaction. For the crystallization centers obtained in supersaturated solutions and in undercooled melted substances, the orientation action is considered most significant, while the accelerating effect in autocatalytic reactions is regarded to be governed by the surface action expressed in its ability to activate the catalytic reaction. The accelerating action of mercuric iodide in the interaction of mercury and iodine (2) and that of newly formed copper in the reduction of copper oxide in which the metallic copper activates the reducing hydrogen are used as illustrative examples.

### Inhibitors of the Anti-detonator Type

Similar to the action of inhibitors and anti-oxygenic agents is that of anti-detonators or anti-knock substances. Anti-detonators are agents counteracting detonation and retarding the velocity of gaseous combustion.

They oppose the interaction of fuel and oxygen and are generally substances which decompose readily to a cloud of solid particles. It is known that the combustion of fuel in internal combustion engines is either detonating or non-detonating. The detonation phenomenon in the combustion of gases occurs under certain conditions. Characteristic of detonation is a definite velocity in the transmission of chemical activity throughout the gas phase. This velocity is the velocity of sound<sup>86</sup> attained under a critical pressure which controls the combustion. The detonation phenomenon was claimed to be induced by certain organic compounds to a varying degree. Ethyl compounds of bromine, oxygen and sulfur, as well as the more simple ethyl compounds, were found to produce a relatively small detonation, while alkyl nitrates and nitrites<sup>87</sup> caused violent detonation when introduced into a fuel-air mixture. The ability to effect detonation has been ascribed to one atom in the molecule, modified to a great extent by the radicals or groups attached to it. The substance inducing detonation must be either mixed with the intake air, or dissolved in the fuel. The mechanism of the detonating reaction has been thought to be that of a modified chain reaction<sup>3</sup> in the sense that it contains not a single center but a group of centers corresponding to "microchains." The smallest amount of localized energy necessary for the spreading out of microchains was regarded as conditioned by the fact that the energy transmitted from the molecule of the reacting substance to a molecule of the decomposition product must exceed the activation energy of the molecule.

Various theories have been proposed accounting for the effect of anti-detonators in counteracting detonation. Each theory presents a different viewpoint as to the significance of an inhibitor in its effect on detonation. One mechanism of the anti-detonator-inhibitory gas was the formation of a shell<sup>138</sup> around the metal in the presence of which the combustion of the explosive mixtures takes place; thereby isolating the metal from the explosive mixture.

Another theory held that if the edges and sharp points left on the walls of the combustion chamber are places with high temperatures accelerating combustion to the detonation stage,<sup>64</sup> then a deposition of lead resulting from the decomposition of the anti-detonator, *e.g.* tetraethyl lead, on these edges and sharp points would make them ineffective. This hypothesis has been opposed<sup>104</sup> by stating that if the effect of suppression is merely due to a covering of edges and sharp points on the inside walls of the chamber, then the effect would be greatly prolonged after the addition of the anti-knock has been discontinued instead of ceasing immediately.

The inhibiting action of ethylene, methane and nitric oxide in the production of a phosphorescent flame in carbon disulfide has been related to the formation of a gaseous film around the "nodes of the reaction."<sup>44</sup> These "nodes of reaction" are assumed to be made up of carbon and sulfur, a product resulting from the partial combustion of carbon disulfide. The action of the carbon-sulfur compound as a nucleus is retarded by the inhibitor condensed on its surface in the early stages of formation. Once

the aggregate is permitted to grow to a relatively large size, the inhibitor may be sufficient to prevent further condensation of carbon disulfide molecules on its surface.

To explain the mechanism of metallic anti-detonators, the assumption of deposition of a metallic film<sup>28, 33</sup> around the nuclear particles of the hydrocarbon so as to prevent a subsequent auto-oxidation has been advanced. If at a definite stage in the cycle of an engine a large number of nuclei centers are established, promoting a uniform oxidation of the fuel throughout the mass, then the suppression action of anti-detonators may be likened to an auxiliary ignition system having the tendency to oxidize the fuel before the action of the actual flame front in the region of hot and highly compressed gases. The film theory was opposed in the statement<sup>104</sup> that colloidal suspensions of certain metals, such as lead and nickel, in motor fuels possess no anti-knock property; but the particles formed by the decomposition of metallo-organic compounds serving as anti-detonators may be temporarily activated and superior to those of other origin.

Another mechanism by which anti-detonators were supposed to act in agreement with Perrin's radiation theory is that in which the inhibitors of the anti-detonator type function as a "screen" adsorbing active radiations<sup>88</sup> necessary to insure the propagation of detonation in the gases and to control the velocity of the movement of the flame. The fact that anti-detonators decompose with the formation of readily oxidizable particles which, by virtue of their heat of combustion, induce a partial combustion of gases in their immediate vicinity, is believed explanatory for the difficulty in the propagation of the flame, the partially burnt gases<sup>33</sup> hindering its progress.

A question has also arisen as to whether anti-detonators influence ionization. Anti-knock compounds were considered<sup>145</sup> present in advance in the flame front and as adsorbers of electrons or ions<sup>101</sup> which are the direct cause of detonation. That ions do play an important role in the propagation of a flame was confirmed experimentally<sup>83</sup> with a mixture of hydrogen, air, benzene, acetylene, etc., in the initial phase of an explosion wave preceding the actual explosion. It appears certain that the propagation and condensation of ions through an explosion wave actually does take place. At every point where there is an increase in velocity the number of ions is greater than at points where there is a decrease in velocity. The removal of ions by imposition of an electric field on a benzene-air mixture was found to prevent its explosion, indicating thereby that ions play an important part in the propagation of an explosion wave by virtue of inducing combustion. The solid particles formed by the decomposition of the anti-detonator are believed to trap a number of ions, causing a decrease in the velocity of combustion of the explosive gaseous mixture.

Many investigations were carried out on explosion limits, regions and spaces, to solve the problem of gas explosions. The influence of many substances on the lower limits of inflammability has been studied quantitatively.<sup>29, 127a</sup> The existence of auto-oxidation boundaries of phosphorus and sulfur has been recognized in estimating the lower limits of inflamma-

bility of phosphorus vapor in oxygen.<sup>65, 68</sup> The lower auto-oxidation boundary pressure was stated to be the upper limit of inflammability. The existence of two explosion limits in explosive gas mixtures has been proved by Hinshelwood and Semenov. The inflammability limits 4.1 per cent and 14.2 per cent were found for a methane-air mixture. About 1.75 per cent of isobutyl chloride vapor was sufficient to prevent the explosion by a spark of a 10 per cent methane-air mixture, and 2.5 per cent propyl bromide vapor sufficed to render the same mixture non-explosive, while 7.5 per cent propylbromide vapor rendered all methane-air mixtures non-inflammable. The explanation for the retardation action has been based on the principle of chain reactions;<sup>31, 32, 68a, 127a</sup> it is assumed that the chain is broken by molecules of the inhibitor which may also be oxidized at the same time.

Anti-knock compounds were classified according to the value of their anti-knock coefficient:<sup>33</sup>

Table 14. Classification of Anti-knock Compounds (Church, Mack and Boord).

Anti-knock Compound	Formula	Anti-knock Coefficient
<b>Lead:</b>		
tetraethyl.	$\text{Pb}(\text{C}_2\text{H}_5)_4$	100.00
tetraphenyl.	$\text{Pb}(\text{C}_6\text{H}_5)_4$	59.0
diethyldichloride.	$\text{Pb}(\text{C}_2\text{H}_5)_2\text{Cl}_2$	67.0
diphenyldimethyl.	$\text{Pb}(\text{C}_6\text{H}_5)_2(\text{CH}_3)_2$	97.0
diphenyldiethyl.	$\text{Pb}(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_5)_2$	93.5
diphenyldichloride.	$\text{Pb}(\text{C}_6\text{H}_5)_2\text{Cl}_2$	72.0
diphenyldibromide.	$\text{Pb}(\text{C}_6\text{H}_5)_2\text{Br}_2$	60.0
diphenyldiiodide.	$\text{Pb}(\text{C}_6\text{H}_5)_2\text{I}_2$	80.0
triparaxylyl.	$\text{Pb}(\text{C}_8\text{H}_9)_3$	64.7
ethylxanthogenate.	$\text{Pb}(\text{C}_2\text{H}_5)_2 \cdot \text{OCS}_2$	7.1
thio-acetate.	$\text{Pb}(\text{CH}_3\text{COS})_2$	8.4
<b>Bismuth:</b>		
triphenyl.	$\text{Bi}(\text{C}_6\text{H}_5)_3$	18.2
triethyl.	$\text{Bi}(\text{C}_2\text{H}_5)_3$	20.2
trimethyl.	$\text{Bi}(\text{CH}_3)_3$	20.2
<b>Tin:</b>		
stannic chloride.	$\text{SnCl}_4$	3.5
stannic iodide.	$\text{SnI}_4$	12.8
diethyl-iodide.	$\text{Sn}(\text{C}_2\text{H}_5)_2\text{I}_2$	12.3
<b>Cadmium:</b>		
dimethyl.	$\text{Cd}(\text{CH}_3)_2$	1.05
<b>Titanium:</b>		
tetrachloride.	$\text{TiCl}_4$	2.7
tetra-iodide.	$\text{TiI}_4$	2.7
<b>Antimony:</b>		
triphenyl di-iodide.	$\text{Sb}(\text{C}_6\text{H}_5)_3\text{I}_2$	4.0
<b>Arsenic:</b>		
monophenyl arsine.	$\text{AsH}_2(\text{C}_6\text{H}_5)$	1.2
triphenyl arsine.	$\text{As}(\text{C}_6\text{H}_5)_3$	1.4
triphenyl arsonium iodide.	$\text{As}(\text{C}_6\text{H}_5)_3\text{I}$	0.7

The effectiveness of anti-knock compounds was assumed to be determined by various factors<sup>33</sup> such as: (1) a resistance to direct oxidation

in air. Lead, selenium, and tellurium compounds and nickel carbonyl were emphasized as most effective anti-knock compounds. The organo-metallic compounds of arsenic, antimony, bismuth, tin and cadmium, however, possess a tendency toward oxidation and are less effective anti-knock compounds; (2) the volatility (boiling point or high vapor pressure under 400°C.), together with the manner of decomposing when heated in air at 200–300°C.; (3) a high temperature in the oxidation of the metal, as compared with ignition temperatures of fuel; and (4) the degree of dispersion of anti-knock compounds to the extent that colloidal dispersion favors rapid oxidation.

The decrease in the effectiveness of an anti-knock compound as seen in the comparison of lead tetraethyl with lead diphenyldichloride and lead diphenyldibromide has been accounted for by a partial internal oxidation due to the halogen-lead linkage which has a tendency to decrease rather than to destroy the anti-knock property.

Egerton<sup>48'</sup> assumes that the use of lead tetraethyl as an "anti-knock" substance in the detonation of petroleum-air mixtures in internal combustion engines may be explained through the role of intermediate peroxides produced in the combustion process.

The anti-knock effect of aromatic amines was found to be similar to that of organo-metallic compounds but, in this case, the hydrocarbon radical attached to the nitrogen atom oxidizes more readily than the fuel itself. An amino-nitrogen atom converts such substances into unstable compounds. Midgley found that diethyl telluride was twenty-five times more effective than ethyl iodide and that the same comparative effectiveness held for their respective phenyl compounds. The relative anti-knock effect of ethyl and phenyl compounds, as determined by Midgley, is shown in Table 15.

Table 15.

Element	Ethyl Compound*	Phenyl Compound
Iodine.	1.09	0.88
Selenium.	6.9	5.2
Tellurium.	26.8	22.0
Oxygen.	-0.036†	0.122

\* Reciprocal of number of gram molecules required to give anti-knock effect equivalent to one gram molecule of aniline; aniline up to 3 per cent by volume in kerosene.

† Induces detonation.

A study of the inhibition factor in catalysis identified not only the types of reactions in which inhibition is observed most frequently, but also the major groups of inhibitors so far recorded. Table 16 shows that inhibitors are most frequently met with among organic compounds after which come the oxides, elements, chlorides, sulfates and hydroxides.

Table 17 permits the rough conclusion that the inhibitor and the catalyst which it inhibits are, in general, in respect to crystal type not isomorphous.

The major problems which become apparent from a logical survey of catalyst inhibitors are the determination of: (1) whether a general mechanism for all inhibited catalysis is possible; (2) whether definite

Table 16.

**Inhibitors****Elements**

O <sub>2</sub> polym. 10.9	As trig. 13.0	Hg hex. 13.7	P trig./cub. 15.4	O <sub>3</sub> ~8
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**Oxides**

H <sub>2</sub> O	FeO	CuO	CaO	MnO <sub>2</sub>	CU <sub>2</sub> O	WO <sub>3</sub>	2NO
hex.	cub.	tricl.	cub.	tetrag.	cub.	tricl.	
19.3	11.8	12.0	16.7	17.0	23.1	31.2	38.2

**Hydroxides**

Ni(OH) <sub>2</sub>	Cd(OH) <sub>2</sub>	Mg(OH) <sub>2</sub>
hex.	hex.	hex.
51.15	57.3	58.4

**Sulfates**

SO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	FeSO <sub>4</sub>
	hex.	rhomb.
33.5	45.2	45

**Chlorides**

HCl	FeCl <sub>2</sub>	SnCl <sub>2</sub>	FeCl <sub>3</sub>
cub.	trig.	rhomb.	hex./trig.
23.7	39.5	47	55.1

**Organic Compounds**

Name	Formula	Crystalline form
Carbon monoxide.	CO	
Methyl alcohol.	CH <sub>3</sub> OH	
Ethyl alcohol.	C <sub>2</sub> H <sub>5</sub> OH	
Isobutyl alcohol.	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> OH	
Glycerol (glycerin).	HOCH <sub>2</sub> CHOHCH <sub>2</sub> OH	
Benzyl alcohol.	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	
Mannitol.	CH <sub>2</sub> OH(CHOH) <sub>4</sub> CH <sub>2</sub> OH	rhomb.
Ethyl ether.	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	rhomb.
Turpentine.		
Arabinose.		rhomb.
Glucose.		rhomb.
Maltose.		
Phenols.		
o-Nitrophenol.	NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OH	rhomb., needles.
Thymol.	CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> (OH) <sub>2</sub>	monocl. needles.
Oxalic acid.	COOH · COOH	hex. plates.
Benzoic acid.	C <sub>6</sub> H <sub>5</sub> COOH	monocl.
Salicylic acid.	HO · C <sub>6</sub> H <sub>4</sub> · COOH	monocl. leaf.
Gallic acid.	(HO) <sub>3</sub> · C <sub>6</sub> H <sub>2</sub> · COOH	monocl.
Tannic acid.	C <sub>12</sub> H <sub>10</sub> O <sub>5</sub>	monocl.
Diphenyl ethylene.	C <sub>6</sub> H <sub>5</sub> NHCH <sub>2</sub> CH <sub>2</sub> NHC <sub>6</sub> H <sub>5</sub>	
Furfuryl ethylene.	C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	
Trihydroxybenzene (pyrogallol).	C <sub>6</sub> H <sub>3</sub> (OH) <sub>3</sub>	
Citric acid.	COOH · CH <sub>2</sub> C(OH)(COOH)CH <sub>2</sub> COOH	rhomb.
Acetic acid.	CH <sub>3</sub> COOH	liq.
Trichloroacetic acid.	CCl <sub>3</sub> COOH	rhomb.
Quinol (hydroquinone).	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	hex.
Catechol (pyrocatechol).	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	monocl.
Resorcinol.	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	rhomb.
Guaiacol.	CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> OH	hex. prisms.
α- or β-Naphthol.	C <sub>10</sub> H <sub>7</sub> OH	monocl.
o- or p-Nitrophenol.	NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OH	monocl.
α-Naphthylamine.	C <sub>10</sub> H <sub>7</sub> NH <sub>2</sub>	rhomb.
Luminal.	NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	rhomb.
Urotropin	NHCON — HCOC(C <sub>2</sub> H <sub>5</sub> ) (C <sub>6</sub> H <sub>5</sub> ) CO	
(hexamethylenetetramine).	(CH <sub>2</sub> ) <sub>6</sub> N <sub>4</sub>	rhomb.
Caffein	C <sub>8</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>	
(1,3,7-trimethylxanthine).		
Brucine.	C <sub>23</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub> · 4H <sub>2</sub> O	monocl. prisms.



Table 17.

Table 17.

Inhibitors for catalyst: Pt cub. 9.03*		Inhibitors for catalyst: Cu cub. 7.05		Inhibitor for catalyst: Ag cub. 10.13	
As trig. 13.0		C <sub>2</sub> H <sub>5</sub> OH 44.7		H <sub>2</sub> O hex. 19.3	
Inhibitors - Elements		Inhibitor for catalyst: CuO monocl. 12.0		Inhibitor for catalyst: Pd	
Co hex. 6.58		H <sub>2</sub> O hex. 19.35		CO trig. 27	
Cu cub. 7.05		Inhibitors for catalyst: CuCl <sub>2</sub>		Inhibitors for catalyst: Pb(OH) <sub>2</sub>	
pure Pt cub. 9.03		HCl cub. 23.7		Ni(OH) <sub>2</sub> Cd(OH) <sub>2</sub> Mg(OH) <sub>2</sub>	
Inhibitors - Oxides		H <sub>2</sub> SO <sub>4</sub> 45.2		51.15    57.3    58.4	
As <sub>2</sub> O <sub>3</sub> trig. 25.7		Inhibitor for quartz:		Inhibitors for catalyst: Al <sub>2</sub> O <sub>3</sub> trig. 25.7	
SO 33.55		H <sub>2</sub> O hex. 19.3		Hg hex. 13.7	
Inhibitors - Halides		Inhibitor for catalyst: Ni cub. 6.55		H <sub>3</sub> PO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	
HBr rhomb. 23.7		50% alloyed Sn		47    45	
HCl cub. 23.7		Inhibitor for catalysts: Ni(OH) <sub>2</sub> or Co(OH) <sub>2</sub>		CuO    CaO    Cu <sub>2</sub> O    WO <sub>3</sub> Co <sub>2</sub> O <sub>3</sub>	
NH <sub>3</sub> 19.6		O <sub>2</sub> or sulfites.		monocl. 12.0    16.7    23.1    tricl. 31.2    39.8	
H <sub>2</sub> S    Ultraviolet rays cub. 26.91		Organic Compounds			
CO trig. 27					

\* Spatial factor, W. Biltz, "Raumchemie der festen Stoffe," Leipzig, Verlag, L. Voss (1934).

physico-chemical characteristics of the inhibitor are responsible for the suppression of the catalytic reaction; or (3) whether the type of the catalytic reaction and the conditions under which it proceeds are of greater significance.

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# Chapter 6

## Promoters and Poisons in Catalysis

### PROMOTERS

#### Introduction

The possibility of choosing a promoter from theoretical considerations would permit one to obtain (a) definite catalytic reactions with definite final products; (b) improvement of processes to insure better yields than those obtained with a catalyst alone, and (c) shifting of the reaction in a more favorable direction.

In order to approach the problem of predicting promoters, a thorough understanding of the following questions is necessary. What is a "promoter"? What are its functions? What mechanism operates in "promoted" catalysis? Is there a certain interrelationship between the action of a promoter and the corresponding catalyst which it activates? Is the choice of a promoter determined by the type of chemical reaction, or is the promoter specific with respect to the catalyst which it promotes?

#### Definition and Functions of a Promoter

When the catalyst is not alone in the system, difficulty arises in distinguishing between the "promoter" and the promoted catalyst. Pease and Taylor<sup>109</sup> suggested differentiating between simple activation of a single catalyst by another substance which in itself is not a catalyst of the reaction, or by a small amount of a relatively active substance, and the "co-activation" of a number of catalysts in which the effect of every active substance is increased by their joint presence. The term "co-activation" has been considered to be related to the term "promotion." As an example of "co-activation," one may consider the synthesis of ammonia with an iron-molybdenum mixture in which both elements serve as catalysts for the reaction; but a mixture of equal parts of iron and molybdenum is more effective than either metal alone. In homogeneous catalysis, for example, in the hydrolysis of esters, the action of salts is considered as simple activation, for the salts themselves have practically no effect. Difficulty in defining a "promoter" lies in the fact that a mixture of two catalysts is not in all cases many times superior in its action. Maxted,<sup>90</sup> studying the oxidation of ammonia and relating the yield to mixed catalysts (Table 1), showed that the catalytic action is not additive.

The effect of a metal support for a platinum or palladium hydrogenation catalyst varies considerably with the nature of the metal. Deposition on nickel and cobalt does not always appreciably affect the activity of platinum or palladium, while iron or copper may act as poisons to platinum or palladium even at elevated temperatures and pressures.<sup>105</sup> A promoter

Table 1.

Catalyst	Yield (%)	Catalyst	Yield (%)
Fe	83.5	Fe + K	83.0
Fe + Bi	94.6	Fe + Sb	82.5
Fe + Cu	92.0	Fe + U	82.0
Fe + Ce	90.0	Fe + Pb	81.8
Fe + W	89.3	Fe + Mn	79.0
Fe + Th	87.3	Fe + Zn	67.0
		Fe + Ca	64.0

is not merely a component of a mixture of two or more substances each of which is a catalyst, or simply a joint catalyst, but rather a substance which increases the activity to an extent exceeding many times the additive effect of the single components of the catalyst mixture. Russell and Taylor,<sup>123</sup> studying the synthesis of methane from carbon dioxide and hydrogen over nickel on pumice, stated that the addition of 0.5 per cent cerium or thorium increases the reaction velocity ten times. Kunsman<sup>80</sup> refers to an eighteen-fold increase in the catalytic activity of the iron catalyst where a promoter is used. In addition, the promoter does not always act in the same capacity as the catalyst. The influence exerted by two catalysts one of which is a promoter may either be directed toward the same effect, thereby effecting a more complete conversion,<sup>60, 62</sup> or, the function of the two catalysts may be specific, each acting as an individual catalyst for one of the successive steps into which the reaction is divided. The increased yield is then the result of separate actions induced by the promoter and the catalyst, both occurring simultaneously.

The divided action of the catalyst and its promoter was recognized early by Ipatieff.<sup>63</sup> He produced evidence for the conversion of camphor into isocamphene by the divided action of catalyst (nickel) and promoter (alumina), the catalyst participating in the hydrogenation of camphor to borneol (320–350°), the promoter dehydrating borneol to camphene (350–360°), and both activating each other, so that the conversion of camphor to isocamphene was carried out in one step at 200°. Ipatieff also combined nickel oxide (catalyst) and alumina (promoter) to hydrogenate fenchone to fenchene in one step (215°C.), using nickel oxide for hydrogenation of fenchone to fenchanol (240°) and aluminum oxide for dehydration of fenchanol to fenchene. Medsforth,<sup>96</sup> studying the hydrogenation of carbon monoxide and carbon dioxide to methane, using nickel catalyst with the addition of dehydrating agents, such as oxides of cerium, thorium, chromium, barium, aluminum, molybdenum and vanadium, considered the reaction as a promoted catalysis with divided action of the catalyst and the promoter. The nickel catalyst assists in uniting gaseous carbon monoxide and hydrogen to form an intermediate compound, methyl alcohol,  $\text{CO} + 2\text{H}_2 \longrightarrow \text{H}_3\text{COH}$ , while the promoter, alumina, for example, assists in the dehydration action:  $\text{H}_3\text{COH} \longrightarrow \text{CH}_2 + \text{H}_2\text{O}$ , after which the reaction is completed as follows:  $\text{CH}_2 + \text{H}_2 \longrightarrow \text{CH}_4$ . There is a selectivity in a promoted reaction which is due to the fact that in the presence of the same catalyst and the same promoter the reaction which is normally slower is accelerated to a greater extent than that which is nor-

mally faster. Carbon monoxide and steam react to form carbon dioxide and hydrogen,  $\text{CO} + \text{H}_2\text{O (steam)} \longrightarrow \text{CO}_2 + \text{H}_2$ , and these in turn react to form methane and water,  $\text{CO}_2 + 4\text{H}_2 \longrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ . The yield of methane is much greater when alumina is used as a promoter for nickel than in the presence of nickel alone.

The promoter not only causes a change in the activity of the catalyst, correspondingly increasing the rate of the reaction beyond that in the presence of the catalyst alone, but it may also prolong the life span of the catalyst so that the process yields the same results without reactivation of the catalyst. In some cases the sharp rise in the activity of the catalyst due to a promoter is followed by a slow fall from the maximum reached;<sup>127</sup> in others, a sharp initial rise in activity is accompanied by its rapid fall.<sup>12</sup> The promoter effect has been explained also by assuming that touching boundaries of neighboring catalysts act as zones of increased reaction velocity. An inlet and outlet of the reaction participants occurs partially through diffusion along the surfaces.<sup>35</sup>

### Concentration of the Promoter; Promotion Factor

The maximum active concentration of the promoter is rather small, and varies. It is not the absolute value of the concentration—the change in surface concentration may be minute—but rather the definite ratio of the promoter to the catalyst which is of major significance in the change of the activity of the promoted catalyst.

The necessity of a proper ratio of catalyst to promoter has been proved in many instances. Medsforth<sup>95</sup> ascertained that the addition of 0.5 per cent cerium to a nickel catalyst increases the reaction rate ten times; in this catalyst one molecule of cerium is present for every 1130 atoms of nickel. In connection with the accelerating effect in the decomposition of hydrogen peroxide in the presence of an iron salt activated by a copper salt promoter, a maximum rate of reaction was obtained with one millimol per liter of the added copper salt; the maximum concentration of the promoter appeared to be independent of the concentration of the catalyst.<sup>27</sup> Hurst and Rideal<sup>61</sup> estimated the influence of the promoter concentration in the selective combustion of carbon monoxide over copper catalysts (Figure 1). Cupric oxide is formed by the interaction of copper and oxygen; cuprous oxide is produced at lower temperatures.

Mittasch,<sup>97</sup> studying the change in activity of a molybdenum catalyst with iron, cobalt, and nickel promoters in the synthesis of ammonia, found that only an excess of molybdenum over the quantity required to combine with nickel gave catalysts of high and persistent activity. When nickel was added in amounts greater than that required to form the compound nickel-molybdenum, the catalyst obtained lost its activity completely in tests of long duration (Figures 2 and 2a). In sodium hypochlorite catalysis,<sup>85, 86</sup> the ratio of copper atoms (catalyst) to magnesium atoms (promoter) show maximum promotion for  $\text{Cu:Mg} = 1:3$  or  $1:4$ ; the promoter effect practically disappears for the ratio  $\text{Cu:Mg} = 1:8$ .

Griffith and Hill<sup>66</sup> related, on the one hand, the activity of molyb-

denum oxide in the decomposition of hexane and cyclohexane ( $500^{\circ}$ ) to the concentration of the silica promoter as shown in Figure 3; on the

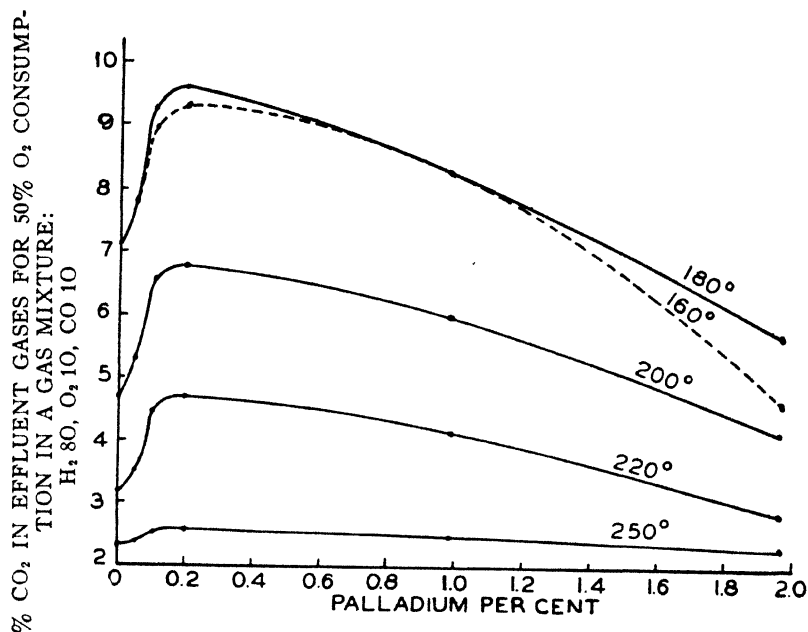


FIGURE 1.

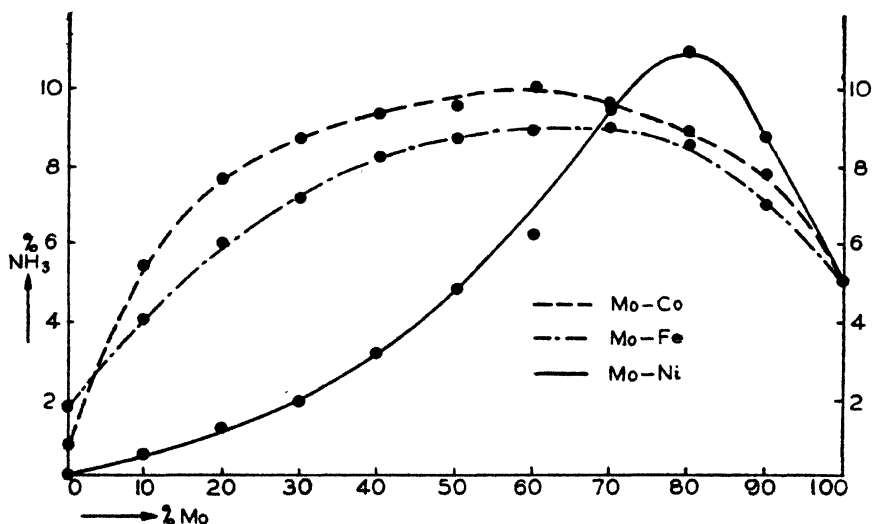


FIGURE 2.—Catalytic Activity of Mo-Fe, Mo-Ni and Mo-Co after 24 hrs. of the Experiment ( $550^{\circ}$ , 200 atm., 50 l. gas per hr., 1 g. metal mixture).

other hand, the change in the amount of the hydrogen adsorbed with the increase in the concentration of the promoter, as shown in Figure 3a.



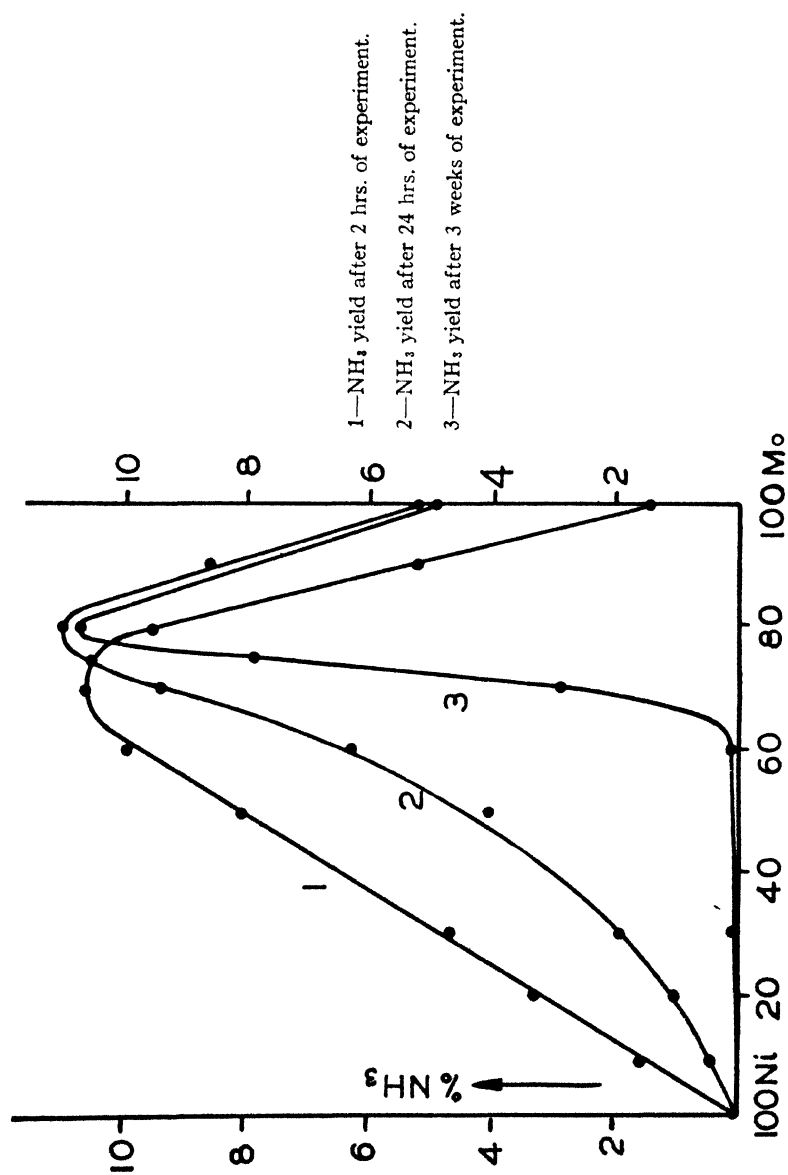


FIGURE 2a.

Later, Griffith<sup>55a</sup> showed that the oxides of sodium, chromium, cerium, aluminum, barium, boron, and thorium also promoted the molybdenum/oxide catalyst, and that their maximum effect was exerted when their molecular concentration was the same as that at which silica was most active; easily reducible oxides, such as those of lead, iron, or copper, were most active as promoters when their concentration was half that of the above substances.

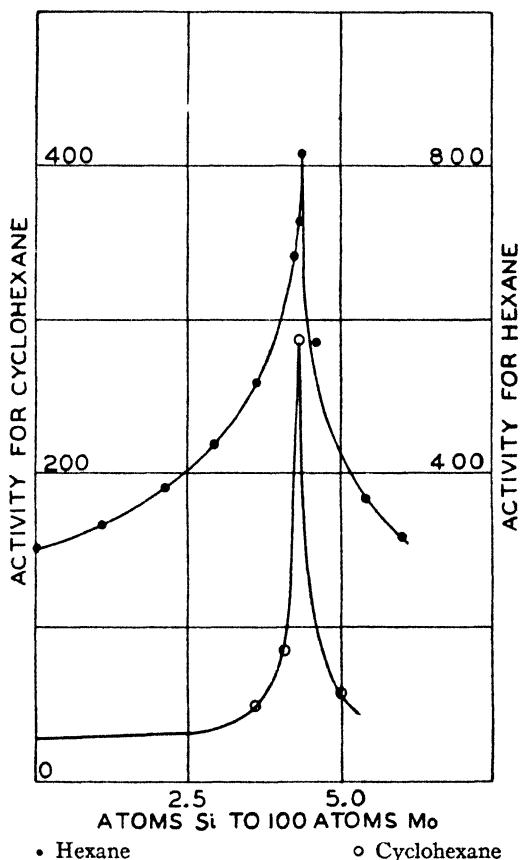


FIGURE 3.—Activity Curve at Low Pressure.

Goggs<sup>53</sup> found evidence for the existence of a critical promoter concentration in the case of carbon monoxide combustion over thorium catalysts with cerium oxide as promoter. Ablesowa and Roginsky,<sup>1</sup> in an investigation of the promoter action of gases upon hydrogenation catalysts, interpreted graphically the catalytic activity as a function of the gas (hydrogen) content in the layer of nickel catalyst. The maximum promotion was found for the ratio  $H_2 : Ni = 1 : 100$ . According to Bloch and Kobosev,<sup>24</sup> in the decomposition of hydrogen peroxide over ferric oxide-aluminum oxide catalysts with varying content of aluminum oxide,

from one to twenty per cent (temperature  $30^\circ$ ), the optimum activity lies in a promoter content of two per cent by weight, activity of pure aluminum oxide being about zero.

The fact that there exists a limit to the accelerating effect of a promoted catalyst led to the idea of a quantitative estimation of the extent of promotion termed "promotion factor."<sup>27, 121</sup> The latter corresponds to

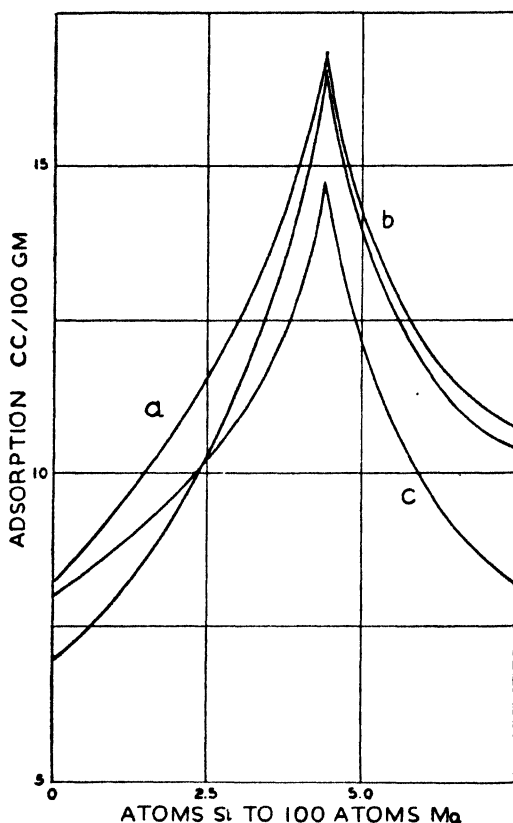


FIGURE 3a.—Hydrocarbon Adsorption at High Temperatures.

- |                |             |
|----------------|-------------|
| a. Hexane      | $400^\circ$ |
| b. Cyclohexane | $450^\circ$ |
| c. Benzene     | $450^\circ$ |

the ratio of the maximum rate of the promoted catalytic reaction and the normal rate for a given concentration of the catalyst and is of importance in the course of comparing two promoters for one and the same system or for comparing promotion effects for different systems. Robertson<sup>121, 122</sup> illustrated the promotion factor graphically as in Figure 4, in which  $F$  denotes the rate of the non-promoted reaction;  $F + D$ , the corresponding rate of the promoted reaction, and  $D$ , the difference between rates in the intermediate stages of the reaction. Furthermore, for any concentration

of the promoter  $P$ , the rate of reaction differs from complete promotion by the amount  $p$ . When more promoter is added,  $p$  changes in proportion

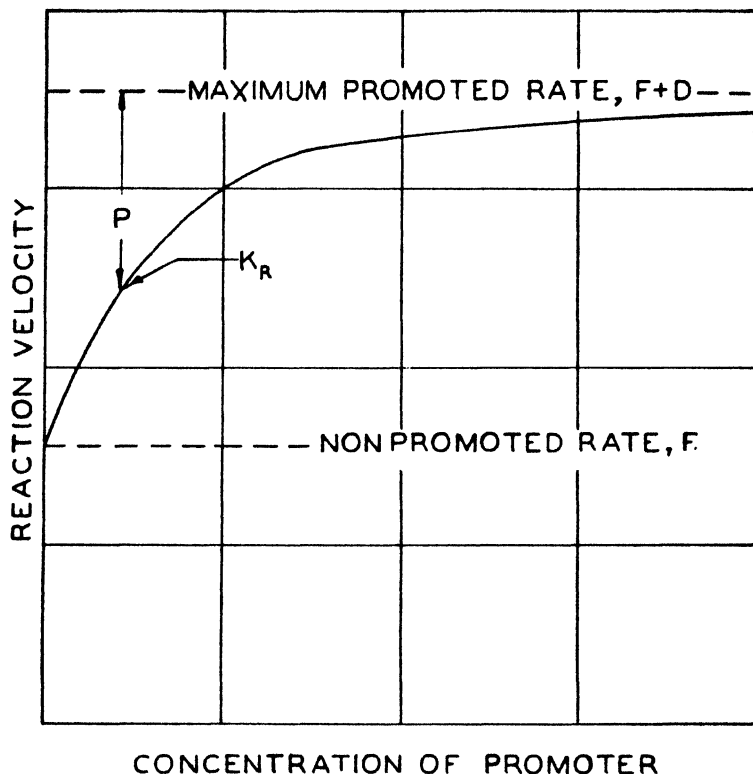


FIGURE 4.

to the amount yet unchanged. Robertson expresses this change in the following equations:

$$-dp/dP = K'p - dp/p = K'dP - \log p = K'p$$

or

$$p = Ke^{-Pk}$$

If  $K$  is equal to  $D$  then the reaction rate  $K_R$  is as follows:

$$K_R = F + D - D_e^{-Pk} = F + D(1 - e^{-Pk})$$

in which  $F$  and  $D$  may be obtained in the form of "promotion factors."

#### Mechanism of the Promoter Action

The action of promoters may be judged from: (a) the mechanism by which the promoter acts; (b) the conditions for promotion, and (c) the interrelationship between the properties of the promoter and the catalyst specific for the particular type of reaction. Various explanations for the mechanism of promoters have been made available, but not one as yet has

been universally accepted. It was supposed that if the catalyst acts by virtue of its ability to form intermediate compounds, then the promoter functions as a secondary catalyst accelerating both the formation and subsequent decomposition of the intermediate product formed between the catalyst and the reactants.<sup>27</sup> In the decomposition of hydrogen peroxide with an iron salt as a catalyst and a copper salt as a promoter the catalyst forms an intermediate compound,  $\text{H}_2\text{FeO}_4$ , while the copper salt accelerates its formation and decomposition. Further, the promoter may not only accelerate the actual velocity of the reaction, but it may function also as a "protector"<sup>10</sup> of the catalyst. If this should be the case, then a linearity of the change in the rate of the reaction in the presence of a promoter is to be expected. The protective action of the promoter was visualized in the ability to inhibit the growth of the crystals of the catalyst due to a very even distribution. Mittasch and Reinecke<sup>98</sup> showed that both  $\alpha$ - and  $\gamma$ -aluminum oxide form mixed crystals with ferric oxide so that when reduction of ferric oxide takes place alumina inhibits the growth of large crystals.

The protective action of the promoter may be expressed likewise in a restoration of the catalyst to its normal function.<sup>106</sup> For example, the accelerating effect of sodium carbonate on the hydrogenation of liquid phenol in the presence of nickel catalyst was considered to be due to prevention of the poisoning effect which otherwise would be caused by nickel phenolate.

Adams and Garven,<sup>5</sup> studying the possibility of directing and controlling the reduction of cinnamic aldehyde by promoted catalysts, found that the promoter action of certain salts in the reduction of aldehydes with platinum oxide or platinum black prevented the poisoning of the catalyst by the highly adsorbed aldehyde by aiding in its desorption. The promoter serves, at the same time, as an activating agent for the substance to be reduced; the aldehyde is not activated for reduction by the platinum catalyst, but by the promoter. Promoters, especially salts of iron and zinc used in the reduction of aldehydes, serve as catalysts for various types of aldehyde reactions, such as the formation of diacyl and acetals. In general, the promoter action in the reduction of aldehydes, is rather complex. Waldschmidt, Leitz and Seitz<sup>140</sup> stated that promoters in aldehyde reduction do not function unless oxygen is present. This suggested the probability that the aldehyde itself is not activated by the platinum catalyst but that an intermediate oxygen complex of the aldehyde is readily activated by platinum and reduced. Therefore, promoters, such as zinc and iron salts, may act as catalysts in the formation of an oxygen-aldehyde complex or as an oxygen carrier from the oxygen-aldehyde molecule, thereby slowing down the reduction of oxygen by hydrogen.

The action of a promoter may be specific in the sense of altering the relative adsorption of reacting components. Cassel<sup>38</sup> suggested that a promoter action takes place when the main component adsorbs one reactant and the promoter another. But this is not in agreement with the observed effects of promoters on the adsorption of reactants. If the action of a promoter were the alteration of the relative adsorption of reacting sub-

stances then either an optimum ratio for the desired interaction would be obtained,<sup>119</sup> the ratio of adsorbed reactants being changed,<sup>23</sup> or a rearrangement of chemical forces in the activated molecules would be effected whereby the promoter would activate one of the interacting substances and the catalyst the other.<sup>21</sup> The action of a promoter in general cannot be estimated by a quantitative surface extension or by a change in the relative concentration of adsorbed reactants. The qualitative adsorption studies of Wyckoff and Crittenden<sup>145</sup> indicate that the function of alumina and potassium aluminate as promoters is in controlling the reduction of the crystalline structure, providing thereby a more extensive surface.

Hurst and Rideal,<sup>61</sup> studying the adsorption of hydrogen and carbon monoxide singly and in mixtures on a copper catalyst with palladium or other metals as promoters, assumed that the action of the promoter was not merely due to a surface extension, but involved the nature of the interface between catalyst and promoter. The promotion action of palladium on the copper catalyst is expressed in an increase in the adsorption of carbon monoxide and in a decrease in the adsorption of hydrogen; in the presence of both gases, the relative increase in the adsorption of carbon monoxide is shown by an increase in the ratio  $\text{CO} : \text{H}_2$ .

Russel and Taylor,<sup>123</sup> investigating the action of thorium on a nickel catalyst in the catalytic interaction of carbon dioxide and hydrogen resulting in the formation of methane and water, found that surface extension as measured by the adsorption of either carbon dioxide or water increased only twenty per cent, whereas ten per cent thorium increased the catalytic activity of nickel ten times. Thus the surface of a promoted catalyst may retain a larger fraction of the total amount of gas adsorbed in a reactive state than that of a non-promoted catalyst. The increased efficiency of a catalyst due to a promoter may be also the result of an increase in the internal area of the catalytic surface.<sup>102</sup> Further, it has been postulated that if the action of promoters is not based on the increase of the reachable surface, it may be provided through a more favorable atomic or molecular configuration of the reactants on the surface of a promoted catalyst.<sup>133</sup>

The mechanism of a promoter action may concern itself also with an increase in the number of active atoms or their groups in the catalyst or be due to a specific change in the nature of active atoms so that a greater number of transformations per unit time may be effected. The ratio of active atoms to the total number of iron atoms in the catalyst used for the synthesis of ammonia was found to be 1 : 2000 for pure iron and about 1 : 200 for iron promoted with alumina or potassium aluminate.<sup>6, 80</sup> It has been found that a larger amount of oxygen can be retained by a promoted catalyst due to the greater number of active (oxidizable) atoms, and that for a given partial pressure of oxygen, the yield of synthesized ammonia is greater with a promoter because of the greater number of unsaturated atoms active enough for the ammonia synthesis but not oxidizable at the given oxygen pressure. Its activity in ammonia synthesis and the ability to form oxides in the presence of low concentrations of water vapor are considered as related properties of iron.

Taylor,<sup>123</sup> discussing the activity of a manganese dioxide-copper oxide

mixture (Hopcalite) in the oxidation of carbon monoxide, considered cupric and manganous ions as oxygen carriers for carbon monoxide having the ability to take up readily the oxygen due to a rapid shifting of electrons in manganese atoms. Similar thereto is the activation action of a promoter which, according to Taylor, affects the "stray" field or the atomic or molecular configuration of the catalyst. The action of a promoter as relating to the activity of catalysts has been considered by Boswell and Bayley<sup>30</sup> with reference to surface films of dissociated water. They believe that the promoter action is due to the increased concentration of charged hydrogens and hydroxyls in the surface film, the promoter enabling the catalyst to retain more charged hydrogens and hydroxyls in the surface film per gram of catalyst than the catalyst alone. This hypothesis was confirmed by experimental evidence in which cerium oxide acted as promoter for the partially reduced ferric oxide and potassium hydroxide for platinum black in the synthesis of ammonia. The increased capacity for retaining dissociated water in the reduced layer was explained by the fact that a promoter facilitates the transfer of oxygen from the interior of the catalyst to the surface. Other supposed functions of a promoter are: (a) with a promoter the catalytic surface film is formed more rapidly by reduction with hydrogen; (b) the promoter reassembles particles scattered throughout the reduced layer around which dissociated water accumulates at higher concentration, and (c) the promoter may increase the stability of the catalytic film at elevated temperatures and prevent the loss of water. The oxides of aluminum and cerium, when heated up to 450°C., have the ability to retain large amounts of water on their surfaces. Alkali hydroxides on the contrary lose all their water at very high temperatures.

Robertson,<sup>121</sup> studying the decomposition of hydrogen peroxide with mixtures of ferric and cupric salts, defined the function of the promoter as a change of the reaction path together with a displacement of the "steady" state of the catalysis. The presence of cupric dioxide was detected by analysis of the absorption spectra and it was considered reasonable to imply that copper acted as a promoter for ferric ions:  $3\text{CuO} + 2\text{FeO}_3 \longrightarrow 3\text{CuO}_2 + \text{Fe}_2\text{O}_3$ . The combined action of ferric oxide and cupric dioxide, an intermediate product formed only in the presence of ferric oxide, is much more energetic in the reduction of hydrogen peroxide than that of ferric oxide alone.

Kubota and Jamanaka<sup>76</sup> explained the mechanism of promoter action by experiments involving the decomposition of methane by water vapor at 1000°, using reduced nickel as catalyst and oxides of aluminum, zirconium, thorium, calcium, cadmium, zinc, or magnesium as promoters. It was assumed that the reaction occurred as follows:  $\text{CH}_4 \xrightarrow{\text{H}_2\text{O}} \text{CO} + 3\text{H}_2 \xrightarrow{\text{H}_2\text{O}} \text{CO}_2 + 4\text{H}_2$ , the function of the promoter being the transference of water molecules to the reaction centers of the catalyst where the action of water on methane takes place.

It has been also conceived that promoters may aid in the formation, as well as in the preservation, of active centers on catalyst particles.<sup>86</sup> Balandin<sup>16, 33</sup> based his explanation for the action of promoters on his multiplet

theory of adsorption, assuming that a promoter action is provided either through the existence of points of attachment for molecules different from those of the original catalyst, or is due to the fact that the active points are better spaced. The promoter acts then by orienting molecules<sup>136</sup> to create a "space" effect in the sense of Langmuir's conceptions.<sup>81</sup> However, experiments by Dubrowskaja and Kobozew,<sup>44</sup> indicated an equality in the activation energy (10,860 calories) for oxygen adsorption for promoted (ten per cent aluminum oxide) and non-promoted ferric oxide and led them to the conclusion that the adsorption centers in both cases are ferric oxide molecules.

If isolated molecular units have a higher reactivity than the substance as a whole, then the increase in reactivity of a promoted catalyst may be due to the fact that the promoter separates small parts of the catalyst mass.<sup>82</sup> The mechanism by which a promoter acts has been connected with the nature of the interface between the catalyst and the promoter. The maximum promotion was assumed to occur when every molecule of the catalyst was separated from its neighboring molecules by a definite number of single molecules of the promoter so as to prevent coalescence.<sup>46, 85, 86</sup> Water molecules prevented the coalescence of iron atoms in the synthesis of ammonia. Likewise, magnesium oxide prevented the coalescence of copper oxide in the experiments of Lewis.<sup>86</sup>

The action of a promoter was related to the existence of layers on the surface of a catalyst, each layer having its own activity. The number of such layers was considered to be limited and determined by measuring the adsorption of gases. It is believed that the promoter changes the magnitude of individual surfaces and increases the value of every surface to a different extent.<sup>57</sup>

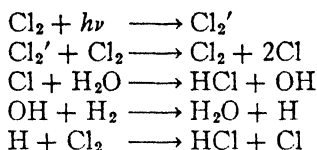
Kostelitz and Hüttig,<sup>75a, 75b</sup> studying the decomposition of methanol over mixed catalysts CuO and ZnO (prepared as pressed tablets under 50–1000 atmospheres' pressure at 270–320°), considered two kinds of promoter effects: (1) "structural promotion" and (2) "synergetic promotion". The structural promotion in the case of Cu-rich preparations of the ZnO series means that ZnO incorporated in between the CuO particles prevents Cu originating at high temperatures through reduction, from sintering together into large aggregates, and thereby decreases its catalytic activity. In favor of this interpretation of the structural promotion are (1) the appearance, (2) the smaller percentage of shrinking and (3) great drop in the tenacity of the catalyst at and after catalysis.

The "synergetic promotion" is interpreted in the sense of formation of specifically acting fields of forces at the Cu-ZnO phase boundaries, to which an essential significance is ascribed with respect to catalytic activity. Although both promotion effects are present at the same time, the synergetic promotion is clearly expressed when the part of ZnO is so large, or respectively the part of Cu so small, that by a far-reaching prevention of sintering maximum effects do not occur.

Coehn and Jung<sup>37</sup> showed that water increases the velocity of chemical reactions. Investigating the relationship between the concentration of water vapor and the rate of hydrogen chloride synthesis, they found that



the velocity increased from zero at  $10^{-7}$  mm. to a maximum value of about  $10^{-5}$  mm.; above this value the velocity was independent of the pressure of water vapor. From these results Coehn and Jung concluded that in all probability water participated in the reaction chain, the reaction investigated being expressed as follows:



Gedye<sup>49</sup> considered the fact that water had no effect on the reaction at higher concentrations; Bodenstein's results, likewise, seemed to disprove evidence for the mechanism proposed. Weigert and Kellermann<sup>142</sup> modified Coehn and Jung's viewpoint by assuming that water enters into a complex before the formation of a chain, thus enabling the reaction to begin with a smaller quantum than would otherwise be the case. Norrish<sup>103</sup> disproved Weigert's theory by showing experimentally that the reaction is probably initiated at a surface upon which water vapor is adsorbed. A somewhat similar explanation in which the water molecules induce a greater chemical reactivity within their sphere of action was proposed by Cathala.<sup>36</sup>

The surface theories for the interpretation of the action of water as promoter were opposed by those who suggested an "ionization" theory. The latter attributed the activation of a reaction to the formation of ions generated in a primary reaction and in turn adsorbed by inactive molecules which they activate, producing a high quantum yield. Baker<sup>15</sup> suggested that ionic nuclei of high specific inductive capacity are formed by water and condensed on ions and electrons as reaction centers. The reaction centers were also thought to be clusters of ions, as illustrated by an ammonia-hydrochloric acid reaction,  $\text{H}_3\text{O}^+$  (hydrated hydrogen) ion and the  $\text{Cl}^-$  ion surrounded by a layer of ammonia molecules. Lind, in his work on the chemical effects of  $\alpha$ -particles, proved the existence of such ion clusters. The formation of these about water molecules may account for the fact that the presence of traces of water accelerates a reaction. Gedye,<sup>49</sup> interpreting the action of water as a promoter, believed that in some cases it is due to absorption and deformations on surfaces, while in other cases it causes a formation or a stabilization of ionic reaction centers. Which of the theories is applicable must be decided for each individual case in which water has an accelerating effect as the influence of water is not the same in all cases.

### Requirements of a Promoter

Certain conditions were postulated as necessary for the occurrence of the promotion effect. It was assumed that promoters are formed if they are able to build mixed crystals with the catalysts which they promote.<sup>85, 86</sup> Abnormally small densities and indistinct x-ray spectra or complex surfaces were considered to account for this fact.<sup>13</sup> The promoter action of aluminum oxide upon iron in the synthesis of ammonia has been interpreted on the

assumption that iron finely dispersed in an internal mixture with small amounts of the mixed crystals, ferrous meta-aluminate,  $\text{FeO} \cdot \text{Al}_2\text{O}_3$  (spinel type), contains little or no dissolved oxygen which may poison the iron in the catalytic reaction. So long as the formation of a spinel takes place, aluminum oxide protects the iron from poisoning, for it frees iron from oxygen. The promoter action of aluminum oxide, with respect to cobalt and nickel, is likewise explained by their ability to form spinel-like compounds, such as  $\text{Al}_2\text{O}_3 \cdot \text{NiO}$ ,  $\text{Al}_2\text{O}_3 \cdot \text{CoO}$ .<sup>124</sup> In the oxidation of oxalic acid, using charcoal as catalyst and nitrogen and iron as promoters,<sup>120</sup> the appearance of two new types of catalytically active surfaces has been made responsible for the promotion effect. These are an Fe-C-N complex surface with a specific activity of about eight hundred times that of the original active carbon surface, and an Fe-C surface with a specific activity of about fifty times that of the original surface; the influence of surfaces such as C-C, C-N, C-Fe had no effect upon the catalytic activity. The x-ray investigation<sup>100</sup> of promoted and non-promoted iron nitride (aluminum oxide, promoter) revealed that the promoter prevents the close union of crystallites. In the non-promoted nitride, as a result of tight packing, the contact or the binding surface of crystallites is considerably greater and therefore the free surface is smaller. A study of the influence of lattice types<sup>88</sup> of a series of mixed crystals, Ni-Fe, Ni-Co, Ni-Cu and Fe-Co (prepared under similar conditions) upon their catalytic activity when used in hydrogenation of benzene into cyclohexane proved that the lattice constant and the lattice type of mixed crystals depend upon the composition of the mixture and the nature of the components. Also that mixed crystals containing face-centered lattice are catalytically active, while those with body-centered lattice are inactive. This is contrary to the statement made by Medsforth<sup>95</sup> whose x-ray investigation established the fact that neither the greater nor the lesser activity of a metal bears any relation to the difference in the structure of metallic crystalline lattices.

Baly's explanation<sup>18</sup> for the enhancement of the efficiency of a catalyst by thorium was that the "surface potential" of nickel oxide, cobaltous oxide and ferric oxide containing thorium oxide are periodic functions of their thorium oxide content. In the case of nickel oxide and cobaltous oxide, minimum surface potentials are exhibited when the molecular proportions are one molecule of thorium oxide to 24 and certain even multiples of 24 molecules of nickel oxide or cobaltous oxide. With ferric oxide the minima are obtained when molecular proportions are one molecule of thorium oxide to 12 and certain multiples of 12 molecules of ferric oxide. The covering power of cobaltous oxide was found to be increased by one-sixth when it contained one molecule of thorium oxide to 24 molecules of cobaltous oxide, and it was therefore concluded that one molecule of thorium oxide replaces 4 molecules of cobaltous oxide in the crystal lattice. When thorium oxide is present in these molecular proportions, it promotes essentially the growth of crystal units and acts as a nucleus for crystal lattice formation. It was ascertained that nickel oxide had the maximum efficiency when it was not dispersed, and distorted by the presence of adsorbed alkali or other electrolytes. Since thorium oxide promotes the growth of the crystal units

thereby decreasing the amount of adsorbed impurities, it should also increase the efficiency of nickel oxide as a catalyst.

The ability to form spinel compounds or complexes at various ratios of the promoter to the catalyst, causing a higher catalytic activity, is not a general property for all the oxides used as promoters. In the catalytic decomposition of sodium hypochlorite solutions<sup>87</sup> the oxides of calcium, cadmium, mercury, magnesium and barium; the carbonates of calcium and barium; barium sulfate, barium oxalate, calcium oxalate, and barium chromate, serve as promoters for copper oxide catalyst, and a maximum promotion was obtained with various ratios of the promoter to the catalyst without any indication of a relationship between the crystal structure of the promoter and its activity.

Kobosew and co-workers,<sup>74</sup> studying the promoter action of aluminum oxide and magnesium oxide on an iron oxide catalyst for ammonia reactions, likewise reached the conclusion that the assumption of the formation of mixed crystals does not suffice in itself to explain the promotion effect. They considered the promotion effect to be a function of the surface activity of substances which serve as promoters. A sharp difference between the surface tension of ferroso-ferric oxide alone and when promoted by two to three per cent of aluminum oxide was established. No promotion effect was found by comparing ferrous oxide and ferrous oxide plus magnesium oxide, because magnesium oxide, although highly isomorphous with ferrous oxide, possesses no surface activity with regard to the catalyst. This is in agreement with the catalytic activity of iron formed by the reduction of these two oxides ( $\text{Fe}_3\text{O}_4$  and  $\text{FeO}$ ). The surface activity of aluminum oxide has been determined through the reflection of slow electrons on promoted and non-promoted iron oxide.

Among the oxides investigated by Gernet and Chitun<sup>50</sup> (those of calcium, magnesium, strontium, zinc, aluminum, bismuth, manganese, nickel, cobalt and copper) not all added to the catalyst  $\text{Cr}_2\text{O}_3\text{-SnO}_2$  in the catalytic oxidation of sulfur dioxide proved to be promoters. Barium oxide and ferric oxide clearly activated the catalyst. The alkaline earth oxides showed an increase in their negative effect with decrease in their ionic radius, that is, when the force of their deforming action upon the field of the catalyst increases. For the oxides of the elements with an even atomic number a smaller negative influence is observed than for elements with uneven atomic numbers. Palmer<sup>106</sup> considered the possible peptizing action of metal oxide promoters on copper catalysts. The promoter aluminum oxide influences the surface activity of the catalyst; being surface active, it decreases the surface tension of the catalyst by forming skins or films in the interface reduced metal/metal oxide. The activity of mixed crystals formed when the ratio of the components  $\text{Ni} : \text{Al}_2\text{O}_3$  as 1 : 1 (each component accelerating a particular reaction as in the dehydrogenation and the dehydration of isoamyl alcohol) has been found from activation energies to have values which remain constant for a great number of experiments. This led to the conclusion that the catalytic activity is localized in the boundary of the mixed crystals  $\text{Ni-Al}_2\text{O}_3$ .<sup>17</sup>

Juliard<sup>66a</sup> interprets the effect of promoter oxides in dehydrogenating cyclohexane with Ni catalyst by assuming that, in preparing the catalyst, a mutual adsorption of hydroxide or carbonate micelles of Ni and that of the metal acting as promoter takes place, and that an activation of Ni particles through the oxide as well as simultaneous activation of oxide particles through Ni occurs. On the basis of this assumption an equation for the catalytic activity of a binary mixture is derived. The heavy metals are to be considered with the hydrogenation catalysts. The light metals alone are little used, but their significance is: (1) as promoters in the two substances mixed catalysts and (2) as agents serving to increase the actual surface contact, from which they may be removed again by a solvent. The oxide and sulfide catalysts are more resistant to heat and poisoning than are metals.<sup>143a</sup>

Kobosew<sup>73</sup> believed that the surface of ferroso-ferric oxide crystals is screened by a layer of aluminum oxide molecules formed as the result of the surface activity of the promoter and consequently the reduction velocity of the magnetite is decreased. One per cent aluminum oxide was found<sup>44, 101</sup> to decrease the reduction velocity of ferroso-ferric oxide up to 80 per cent, and one to two per cent of aluminum oxide and beryllium oxide prevented the reduction of ferroso-ferric oxide catalyst up to 70–90 per cent in the synthesis of ammonia.<sup>73</sup>

The mechanism of a film formation in the interface which prevents the reduction of the metal oxide catalyst thus postulated definite properties of the promoter as well as conditions for promotion: (a) The promoter is assumed to have a peptizing action upon the catalyst forming with it a solid solution of the spinel type ( $\text{BeFe}_2\text{O}_4$ ) ( $\text{MgFe}_2\text{O}_4$ ), or a structure similar to the olivine type as, for example,  $\text{BeAl}_2\text{O}_4$ <sup>48</sup>; (b) The promoter decreases the reduction velocity of the catalyst very strongly and prevents thermal sintering of the reduced catalyst by hindering the growth of crystal units.<sup>125</sup> An x-ray investigation<sup>145</sup> of ammonia-iron catalysts promoted by aluminum oxide or potassium aluminate proved that they maintain a larger catalyst surface by preventing the growth of iron crystals. The crystal lattice is the same as that of the unpromoted catalyst but in the presence of the promoter the reduced iron forms much smaller crystals ( $1 \times 10^{-8} - 1 \times 10^{-3}$  cm.), providing a larger number of active atoms. In addition, the promoter causes the retention of this minute structure for a long time; (c) The adsorption film or skin which the promoter forms in the boundary  $\text{Fe}/\text{Fe}_3\text{O}_4$  is stated to be monomolecular, stable, and retained with great tenacity; therefore, such promoters must be completely saturated oxides, such as aluminum oxide, which have no affinity for oxygen, differing in this respect from the oxides serving as catalysts.

Other investigators have reached similar conclusions. Applebey,<sup>9</sup> discussing the mechanism by which oxides and particularly alumina promote the activity of iron catalysts in the synthesis of ammonia, pointed out that although iron alone is an active catalyst, it rapidly loses its efficiency; the addition of a promoter prevents this loss. The catalyst prepared from  $\text{Fe}_3\text{O}_4$  is more active than that obtained from  $\text{Fe}_2\text{O}_3$ . The use of alumina,

as promoter, is attributed to the isomorphism of ferroso-ferric oxide and  $\text{Fe}(\text{AlO}_2)_2$ , which brings about the essential conditions for the promotion effect, namely, providing barriers of alumina which prevent grain growth or coalescence of active iron centers.

Smith<sup>129</sup> compared the function of alumina as a promoter with that of a carrier for copper catalyst considering Taylor's<sup>134</sup> theory of catalytic surface development in which the high activity of copper on an alumina carrier is emphasized. Smith found that pure copper shrinks on reduction, and the ease of motion of the unsupported copper atoms should leave the surface with few exposed edges and corners. With alumina as the supporting network, shrinkage during preliminary treatment and reduction is slight. The reduced catalyst has a relatively large number of copper atoms in an unsaturated state in which rearrangement of catalyst atoms follows slowly, and is not readily affected by high temperature.

Kagan, Morozow and Podurowskaja,<sup>68</sup> studying the sorption of ammonia over iron catalysts with potassium oxide and aluminum oxide as promoters in the catalytic synthesis of ammonia, reached the conclusion that aluminum oxide adsorbs relatively large amounts of ammonia (at high temperatures, up to 500°, and 10–500 mm. mercury pressure). The relatively great amount of adsorption heat indicates the activation effect. Potassium oxide, on the other hand, decreases the adsorption ability and the adsorption energy of aluminum oxide with respect to ammonia. Thus aluminum oxide retards the velocity of ammonia synthesis as a result of the adsorption of ammonia, while potassium oxide serves to decrease this negative action. The ammonia molecules are adsorbed predominantly by the active centers of the catalyst, covering at the same time the iron and the promoter surface.

A uniformity in the distribution of the promoter throughout the catalyst, resulting in a separation into small units, was assumed to insure an improvement of the catalyst activity. On the other hand, the promoter, to attain its greatest activation effect, was thought to obey the requirement of having many spectrum lines in common with those of the catalyst.<sup>2, 14</sup> The accelerating effect of small amounts of magnesium oxide or manganese dioxide in the dehydrogenating action of copper has been related<sup>106</sup> to a selective adsorption in the infrared region of the spectrum and the process has been considered to be due to radiation. The promoter was supposed to possess a transparency in order that the radiation from the catalyst might be transmitted. From this point of view the promoter's activity may be measured by the reciprocal of a transmission ratio =  $\frac{\text{energy incident}}{\text{energy transmitted}}$ .<sup>75</sup> Furthermore, it has been conceived that a promoter must have a higher adsorbing ability than the catalyst.<sup>106</sup> There have been isolated cases where the hydrogen ion effect on promotion has been observed.

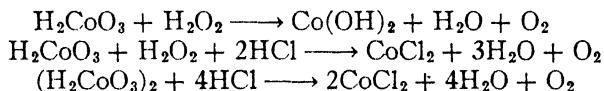
From kinetic measurements and studies of the absorption spectra, it was concluded that a definite hydrogen ion concentration ( $\text{pH} = 4.6$  and  $5.8$ ) is necessary for the promotion effect in the catalysis of hydrogen peroxide decomposition.<sup>122</sup> It was recognized also that the velocity in the thermal

decomposition of ammonia on a "mixed" surface of tungsten and platinum, considered as a promoted catalyst, is greater than on an equal surface of either one of the metals, over a wide range of temperatures. The effect of the promoted catalyst in decreasing the heat of activation<sup>32</sup> is indicated in Table 2.

Table 2.

Catalyst	Heat of Activation cal./gm. mol
Platinum.	130,000
Tungsten.	48,000
Platinum-tungsten.	36,000

As an essential condition for occurrence of promotion, it was suggested that the promoter should differ from the catalytic agent particularly with reference to valence, chemical basicity and greater stability, so that it will be less sensitive toward temperature changes and impurities. An attempt has been made to determine whether the valence of the catalyst is changed during the promotion effect. In studying the promoted catalytic reaction:



Robertson<sup>122</sup> stated that it was impossible to say definitely whether cobalt is in a bivalent or tetravalent form during the promotion action. On the other hand, in the oxidation of sulfur dioxide with vanadium pentoxide catalyst and stannic oxide as promoter, Poljakow<sup>115</sup> attempted to show that the promoter action begins with the formation of vanadium tetroxide by the reduction of vanadium pentoxide followed by a simultaneous precipitation with stannous hydroxide.

It is interesting to note that chemical activity was recognized as dependent on the state in which the components take part in the reaction. Kahlenberg<sup>69</sup> called attention to the fact that ammonia and chemically pure dry hydrochloric acid do not interact with a determinable velocity, while the addition of benzene causes immediate interaction. This investigation assumed that benzene facilitated the formation of a stable colloidal ammonium chloride which assisted catalytically the union of hydrochloric acid and ammonia. Friend<sup>47</sup> applied this catalytic autocolloidal theory to interpret the ability of alloys to act either as promoters or as inhibitors (Ag-Cu, promoter; Ni-Sn, inhibitor) in corrosion processes of ferrous alloys and non-ferrous metals. The fact that alkali carbonates not only fail to inhibit corrosion but on the contrary cause the metal to corrode more rapidly than with distilled water alone was explained by him on the grounds that the alkali when sufficiently concentrated precipitates the catalytic sol as soon as it is formed. Thus the ability of alloys to act either as promoters or as inhibitors in corrosion processes may be connected with the state in which the components participate in the reaction.

Tables 3 to 8 inclusive show various reactions for promoters in catalytic synthesis, decomposition, oxidation, reduction, hydrogenation, dehydrogenation and other miscellaneous reactions.

(Text continued on page 370)

Table 3. Promoters in Catalytic Synthesis.

Reaction	Promoter	Observer
Synthesis of $\text{NH}_3$ with Fe or Mo.	Greater yields of $\text{NH}_3$ obtained by using a mixture of Fe and Mo.	Badische Anilin u. Soda Fabrik: G. P. N5833 (1911).
Synthesis of $\text{NH}_3$ over Fe catalyst; percentage of $\text{NH}_3$ formed per passage	None. 0.2% $\text{K}_2\text{O}$ 1.31% $\text{Al}_2\text{O}_3$ 1.05% $\text{Al}_2\text{O}_3 + 0.26\% \text{K}_2\text{O}$ ; activating effect of an alkali in the presence of $\text{Al}_2\text{O}_3$ is ascribed to its dispersion action, having as result extensive production of Fe-oxide-Al mixed crystals (in systems susceptible to poisoning by S, the alkali may absorb S so that the adsorption of the poison by the catalytic active Fe surface is deflected to a certain extent).	Almquist and Crittenden: <i>Ind. Eng. Chem.</i> , 18, 1307 (1926).
5.49 3.43 9.35 13.85		
Synthesis of $\text{NH}_3$ with iron carbide catalyst.	Cyanides of the alkalies or metals of the alkaline earths.	Müller: E. P. 271, 482, July 13, 1927.
Synthesis of $\text{NH}_3$ with Mo catalyst.	Co, Fe, Ni.	Mittasch: <i>Z. phys. Chem., Bodenstein Festband</i> , 574 (1931); <i>Z. Elektr.</i> , 36, 567, 690 (1930).
Combining of oxygen and hydrogen at 450°C. with $\text{ThO}_2$ catalyst.	Maximum activity with about 1% Ce.	Swan: <i>J. Chem. Soc.</i> , 125, 780 (1924).
Synthesis of $\text{CH}_4$ from $\text{CO}_2$ and $\text{H}_2$ , using Ni on pumice as a catalyst.	10% Th on pumice accelerates catalytic activity of Ni; velocity increased 10 times as compared with catalytic reaction in which no promoter is used.	Russell and Taylor: <i>J. phys. Chem.</i> , 29, 1325 (1925).
Crude oil synthesis from water gas with Co-Cu catalyst.	$\text{CeO}_2$ less desirable as an accelerator than either $\text{MgO}$ or $\text{ZrO}_2$ .	Kodama: <i>Sc. Papers Inst. Phys. Chem. Res. (Tokyo)</i> , 14, 26, 257-259, 13-25 (1930).
Synthesis of liquid hydrocarbons from CO and $\text{H}_2$ over Cu-free cobalt catalysts on kieselguhr as carrier; T. 210°; the activity of Co catalysts is increased considerably through precipitation in the presence of kieselguhr; reduction temperature 250°, 300°, 350°, 400°, and 450°; the decrease of activity by increase of the reduction temperature, which is greatest in case of Co-Mn catalysts and smallest in case of Co- $\text{U}_3\text{O}_8$ , may be strongly decreased through suitable additions of kieselguhr; the activity of Co- $\text{U}_3\text{O}_8$ catalysts is greater than that of Co- $\text{ThO}_2$ catalysts and considerably greater than that of the Co-Mn catalysts.	$\text{ThO}_2$ (18% and 22%). $\text{U}_3\text{O}_8$ (12%). Mn (15%, 20% and 24%) the increase in the promoter content acts qualitatively just like an increase in the carrier content because both make difficult the sintering of the reduced Co; the greater the activity of the promoter-containing catalysts, the smaller is the lowering of their activity by increase of the reduction temperature.	Tsutsumi: <i>Sci. Papers Inst. Phys. Chem. Res. (Tokyo)</i> , 35, 441-46 (1939).

Table 4. Promoters in Catalytic Decomposition.

Reaction	Promoter	Observer
Decomposition of $\text{H}_2\text{O}_2$ by salts of heavy metals as catalysts.	Glass wool.	Elissaffoff: <i>Z. Elektr.</i> , 21, 352 (1915).
Decomposition of $\text{H}_2\text{O}_2$ by salts of Fe as catalysts.	Reaction accelerated by addition of a small amount of Cu salt; optimum effect with 1 millimole Cu salt (sulfate or chloride) per liter solution).	Bohnson and Robertson: <i>J. Am. Chem. Soc.</i> , 45, 25 (1923).
Decomposition of $\text{H}_2\text{O}_2$ by a ferric salt as catalyst.	Cupric salts.	Robertson: <i>Ibid.</i> , 47, 1299 (1925).
Decomposition of $\text{H}_2\text{O}_2$ by $\text{Cu}(\text{OH})_2$ catalyst; alone, slightly active.	Catalytic activity increased 50 times with $\text{Fe}(\text{OH})_3$ .	Quartaroli: <i>Gazz. chim. ital.</i> , 55, 252, 619 (1925).

Table 4 (Continued).

Reaction	Promoter	Observer
Decomposition of $H_2O_2$ by ferric salts.	Reaction accelerated by Cu salt.	Walton and Christensen: <i>J. Am. Chem. Soc.</i> , <b>48</b> (II), 2083-2091 (1926).
Decomposition of $H_2O_2$ by $K_2Cr_2O_7$ .	Cobaltic salts, especially $CoCl_3$ .	Robertson: <i>Ibid.</i> , <b>47</b> , 1300 (1925); <b>48</b> , 2072-2082 (1926).
Decomposition of $H_2O_2$ by $Ag_2O$ .	$Mg(OH)_2$ , $Cd(OH)_2$ and $Ni(OH)_2$ accelerate the reaction.	Quartaroli: <i>Gazz. chim. ital.</i> , <b>57</b> , 234 (1927).
Decomposition of $H_2O_2$ by $K_2Cr_2O_7$ .	Manganese salts.	Robertson: <i>J. Am. Chem. Soc.</i> , <b>49</b> , 1630 (1927).
Decomposition of $H_2O_2$ by salts of hydrazoic acid.	Ferric ions; the positive catalytic action of $Fe^{+++}$ is greater than the negative catalytic action of $N_3^-$ ion.	Oliveri-Mandala: <i>Gazz. chim. ital.</i> , <b>59</b> , 699-702 (1929).
Decomposition of $H_2O_2$ over Cu salts.	Mn salts.	Bobtsky: (Refer to C. 1936 I 8); referred to by Thomas and Kalman; <i>Compt. rend.</i> , <b>202</b> , 1436-1437 (1936).
Decomposition of $NH_3$ on Fe catalysts.	Catalytic activity varies greatly (as much as 18 times) when a promoter is used.	Kunsman: <i>Science</i> , <b>65</b> , 528 (1927).
Decomposition of $KClO_3$ by dust or smoke.	$MnO_2$ particles accelerate reaction.	Roginski and Schultz: <i>Sc. Mag. Chem. Catheder Eka-terinoslav</i> , 189-206 (1926).
Decomposition of $NaOCl$ by alumina as catalyst; no effect.	Ni and Co peroxides; a mixture of the two oxides more effective; maximum effect with 30% Ni.	Chirnoaga: <i>J. Chem. Soc.</i> , 1926, 127, 1693.
Decomposition of $NaOCl$ by CuO as catalyst.	Fe oxide.	Lewis: <i>J. phys. Chem.</i> , <b>32</b> , 1808-1819 (1928).
Decomposition of $NaOCl$ solutions by CuO catalyst.	Mg, Ca, Ba, Hg and Fe oxides; Ba-Sr sulfate, Ca-Ba oxalate and Ba chromate.	Lewis and Seegmiller: <i>Ibid.</i> , <b>37</b> , 917-921 (1933).
Decomposition of hexane and cyclohexane with Mo oxide catalyst.	Silica.	Griffith and Hill: <i>Proc. Roy. Soc. London (A)</i> , <b>148</b> , 194 (1935).

Table 5. Promoters in Catalytic Oxidation.

Reaction	Promoter	Observer
Oxidation of $NH_3$ by Fe oxides.	A mixture of oxides of either rare earth metals or Bi.	Badische Anilin u. Soda Fabrik: <i>Brit. P.</i> 13,838, June 18, 1914.
Oxidation of $NH_3$ .	Te or its compounds and Pb or its compounds.	Badische Anilin u. Soda Fabrik: <i>Brit. P.</i> 7,651, May 21, 1915; <i>Brit. P.</i> 13,298, May 21, 1915.
Oxidation of $NH_3$ by Fe, Ni, Co, Cu, or Pt.	Cu or Ag.	Maxted and Ridsdale: <i>Brit. P.</i> 10,781, July 26, 1915; <i>Brit. P.</i> 126,083, December 4, 1916; <i>Chem. Abs.</i> , <b>13</b> , 2259.
Oxidation of $NH_3$ by Fe catalyst.	Bi, W and Cu activate Fe catalyst. $Fe-Ca < Fe-Mn < Fe-Pb < Fe < Fe-W < Fe-Cu < Fe-Bi$ ; Bi, W, Cu, Th, and Ce activate Fe catalyst, while Ca and Mn decrease its catalytic activity.	Maxted: <i>J. Soc. Chem. Ind.</i> , <b>36</b> , 777 (1917).
Oxidation of $NH_3$ to nitric oxide by Fe catalyst.	Bi or rare earth oxides; 3-4% Bi oxide yielded 95%; optimum temperature, 600°C.	Badische Anilin u. Soda Fabrik: <i>Brit. P.</i> 13,848, June 18, 1914. Maxted and Ridsdale: <i>Brit. P.</i> 126,083, December 4, 1916; <i>Chem. Abs.</i> , <b>13</b> , 2259. Neumann and Rose: <i>Z. anorg. Chem.</i> , <b>33</b> , 51 (1920).



Table 5 (Continued).

Reaction	Promoter	Observer
Oxidation of $\text{NH}_3$ to nitric oxide.	Bi, most active (97% $\text{CoO} + 3\% \text{BiO}$ ).	Maxted: <i>Chem. Age</i> , <b>7</b> , 816 (1922).
Oxidation of $\text{NH}_3$ to nitric oxide by Co oxide catalyst.	Bi oxide.	Scott and Leech: <i>J. Ind. and Eng. Chem.</i> , <b>16</b> , 81 (1924); <b>19</b> , 170 (1927).
Reactions with $\text{NH}_3$ .	$\text{Al}_2\text{O}_3$ , $\text{MgO}$ , or $\text{ZrO}_2$ .	E. I. Du Pont de Nemours and Co.: E.P. 390,809, November 5, 1933.
Oxidation of gaseous $\text{H}_2$ by $\text{NaClO}_3$ , using Pd as catalyst.	Os oxide increases the catalytic activity of Pd 5 times.	Hoffmann and Schneider: <i>Ber.</i> , <b>48</b> , 1585 (1915).
Oxidation of $\text{SO}_2$ ; x-rays, ineffective in dry air.	Presence of moisture slightly increases rate of oxidation.	Clark, McGrath and Johnson: <i>Proc. Nat. Acad. Sci.</i> , <b>11</b> , 646 (1925).
Oxidation of $\text{SO}_2$ , using $\text{Cr}_2\text{O}_3$ - $\text{SnO}_2$ as catalyst at $420^\circ$ ; yield, 99.25%.	$\text{BaO}$ or $\text{Fe}_2\text{O}_3$ ; maximum action with 0.1-0.13 $\text{BaO}$ per 1.0 $\text{Cr}_2\text{O}_3$ - $\text{SnO}_2$ .	Gernet and Chitun: <i>Zh. prikl. Khim.</i> , <b>8</b> , 598-605 (1935). Adadurow and Gernet: <i>Ibid.</i> , <b>8</b> , 606-611 (1935).
Oxidation of $\text{SO}_2$ by a catalyst, $\text{Cr}_2\text{O}_3$ - $\text{SnO}_2$ .	$\text{BaO}$ and $\text{Fe}_2\text{O}_3$ (the promoter action is ascribed to those oxides having a greater ion radius); oxides of alkaline earths introduce a negative influence upon catalysis, increasing with a decrease in the ion radius; thereby the force of their deforming influence on the field of the catalyst increases (a similar effect is obtained with other oxides investigated, namely, $\text{CaO}$ , $\text{MgO}$ , $\text{SrO}$ , $\text{ZnO}$ , $\text{Al}_2\text{O}_3$ , $\text{Bi}_2\text{O}_3$ , $\text{MnO}_2$ , $\text{NiO}$ , $\text{CoO}$ , $\text{CuO}$ ).	Gernet and Chitun: <i>Ibid.</i> , <b>8</b> , 598-605 (1935).
Oxidation of $\text{SO}_2$ by a catalyst, $\text{Cr}_2\text{O}_3$ - $\text{SnO}_2$ ; T. $420^\circ$ ; yield 99.25%; volume velocity, 60; gas conc., 7% $\text{SO}_2$ ; increase in volume velocity to 140 decreases the yield 98.2%.	Maximum action with the following ratio: 0.1-0.13 $\text{BaO}$ per 1 $\text{Cr}_2\text{O}_3$ - $\text{SnO}_2$ .	Adadurow and Gernet: <i>Ibid.</i> , <b>8</b> , 606-611 (1935).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ over $\text{V}_2\text{O}_5$ .	$\text{K}_2\text{O}$ and $\text{Ag}_2\text{O}$ are converted into sulfates with which $\text{V}_2\text{O}_5$ forms a solid solution or mixed crystals (blue color) and this induces a change in valence together with adsorption or desorption of $\text{O}_2$ .	Siebert: <i>Angew. Chem.</i> , <b>50</b> , 319-320 (1937). Siebert: <i>Chem. Fabrik</i> , <b>26</b> , 1-11 (1937).
$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ by Fe or Co, or their respective oxides as catalysts.	$\text{O}_2$ compounds of Cr, Th, U, Be, and Sb.	Badische Anilin u. Soda Fabrik: Brit. P. 2,306, January 28, 1914; <i>Chem. Abs.</i> , <b>10</b> , 287; G.P. 282,782, December 12, 1913; <i>Chem. Abs.</i> , <b>9</b> , 2461.
Oxidation of CO by $\text{MnO}_2$ or $\text{CuO}$ .	Mixtures of these oxides, more efficient—"Hopcalite."	Lamb, Bray and Frazer: <i>J. Ind. and Eng. Chem.</i> , <b>12</b> , 213 (1920).
Oxidation of CO.	A mixture of catalysts $\text{MnO}_2$ and $\text{CuO}$ (Hopcalite) in which $\text{MnO}_2$ is the direct cause of oxidation at low temperature.	Whitsell and Frazer: <i>J. Am. Chem. Soc.</i> , <b>45</b> , 2848 (1923).
Oxidation of CO by $\text{MnO}_2$ or $\text{CuO}$ .	$\text{MnO}_2$ catalyst more effective by the addition of $\text{CuO}$ ; $\text{CuO}$ catalyst more effective by the addition of $\text{MnO}_2$ .	Bray and Doss: <i>Ibid.</i> , <b>48</b> , 2060 (1926).
Oxidation of CO by $\text{ThO}_2$ .	Maximum activity obtained when catalyst contains 0.96% Ce.	Goggs: <i>J. Chem. Soc.</i> , <b>1928</b> , 2667.

Table 5 (Continued).

Reaction	Promoter	Observer
Oxidation of CO with a mixture of CuO and MnO <sub>2</sub> .	1-5% Ce <sub>2</sub> O <sub>3</sub> accelerates rate of reaction.	Green: "Industrial Catalysis," The Macmillan Co., New York, 1928.
Combustion of CO with Cu catalyst.	Pd.	Hurst and Rideal: <i>J. Chem. Soc.</i> , 125, 685 (1924).
Combustion of CO with Th catalyst.	Ce oxide.	Goggs: <i>Proc. Roy. Soc., London (A)</i> , 148, 191 (1935).
Oxidation of CH <sub>4</sub> with free O <sub>2</sub> , using phosphates of Sn, Fe, or Al as catalysts.	Due to presence of CO, 0.13% HCl is added to increase yield of HCHO.	Medwedew: <i>Trans. Karpov. Inst. Chem.</i> , 4, 117 (1925).
Oxidation of CH <sub>4</sub> to HCHO with Ag as catalyst.	Ag and Cu together more effective.	Hochstetter: U.S.P. 1,100,076, <i>Chem. Abs.</i> , 8, 2770; 1,110,289, <i>Chem. Abs.</i> , 8, 3618.
Oxidation of CH <sub>3</sub> OH to HCHO by Ag or Cu.	Reaction more effective with Ag and Cu together than either singly.	Hochstetter.
Oxidation of CH <sub>3</sub> OH to HCHO in the presence of O <sub>2</sub> with Ag, or Cu, or one of the Pt metals, such as Rh, as catalyst.	A mixture of Ag and Cu.	Hochstetter.
Oxidation of (COOH) <sub>2</sub> , using charcoal as catalyst.	N <sub>2</sub> and Fe accelerate catalytic activity of charcoal.	Rideal and Wright: <i>J. Am. Chem. Soc.</i> , 48, 1813 (1926).
Oxidation of butyric acid by H <sub>2</sub> O <sub>2</sub> .	NH <sub>3</sub> , K <sub>2</sub> HPO <sub>4</sub> .	Dakin: <i>J. Biol. Chem.</i> , 4, 77 (1908).
Oxidation of butyric acid with H <sub>2</sub> O <sub>2</sub> by Co as catalyst.	K phosphate more effective than Na phosphate; dialkali phosphates accelerate reaction more readily than mono-alkali phosphates.	Witzmann: <i>J. Am. Chem. Soc.</i> , 48, 202-208 (1926).
Oxidation of formic acid with H <sub>2</sub> O <sub>2</sub> .	Ferrihydroxide catalyst is activated strongly by Cu (Mn, Co, Ni, Zn have no such promotion action); Cu without Fe hydroxide is practically inactive; Fe <sub>2</sub> O <sub>4</sub> of different origin is a weak catalyst, but Cu activates it greatly; the mechanism of the catalyst action is assumed to follow the scheme: Cu'' + H <sub>2</sub> O <sub>2</sub> by conversion in Cu as Cu-O-O-Cu, which rebuilds CuO, dehydrogenates the ferrihydroxide to iron oxide peroxide, and this, under rebuilding of (FeO · OH) <sub>n</sub> , oxidizes formic acid to CO <sub>2</sub> .	Ofelia Belfiors: <i>Gazz. chim. ital.</i> , 68, 405-411 (1938).
Oxidation of glucose.	Na <sub>2</sub> HPO <sub>4</sub> .	Dakin: <i>J. Biol. Chem.</i> , 4, 77 (1908).
Oxidation of CH <sub>3</sub> OH to HCHO by Cu catalyst.	Addition of 0.1% Ce accelerates rate of reaction (space velocity, 1800 at 200°C.); thorium less effective (space velocity 900 at 205°C.).	Ghosh and Bakshi: <i>J. Ind. Chem. Soc.</i> , 3, 415 (1926).
Oxidation of aniline by H <sub>2</sub> SO <sub>4</sub> .	A mixture of CuSO <sub>4</sub> and H <sub>2</sub> SO <sub>4</sub> , more active; an example of two catalysts activating each other.	Bredig and Brown: <i>Z. phys. Chem.</i> , 46, 502 (1903).
Oxidation of <i>p</i> -phenylene diamine and pyrogallol by air.	Reaction accelerated by colloidal Ag.	Luppo Cramer: <i>Phot. Ind.</i> , 25, 968-970 (1926).
Oxidation of a stable mixture of indigotine (indigo), starch, fuchsin and nitric acid.	SnCl <sub>2</sub> and FeSO <sub>4</sub> .	Eymer: <i>Rev. gen. des Mat. color.</i> , 29-30, 352 (1925-1926).

Table 6. Promoters in Catalytic Reduction.

Reaction	Promoter	Observer
Reduction of CO and CO <sub>2</sub> by Ni catalyst.	V, Mo, Zr, Cr, glucinum (Be), Th, Ce oxides, also silica and alumina.	Ipatieff: <i>Ber.</i> , <b>45</b> , 3205 (1912)
Reduction of CO and CO <sub>2</sub> by Ni catalyst.	Dehydrating catalysts; dehydrogenating catalysts, such as Cu, show no effect as promoters.	Medsforth: <i>J. Chem. Soc.</i> , <b>123</b> , 1452 (1923).
Reduction of CO and CO <sub>2</sub> by Ni catalyst 1. $2\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CO}_2 + \text{CH}_4$ 2. $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$ 3. $\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$	Th oxide, Ce oxide.	Ghosh, Chakravaty and Bakshi: <i>Z. anorg. allg. Chem.</i> , <b>217</b> , 277-283 (1934).
Reduction reaction between water vapor and equal volumes of CO and H <sub>2</sub> over Ni catalyst.	Th, Ce, V and alkali.	Chakravarty: <i>Science and Culture</i> , <b>3</b> , 396 (1938).
Reduction of ketones over Raney Ni.	Metals of the Pt group, particularly Pt itself.	Delépine and Horeau: <i>Compt. rend.</i> , <b>201</b> , 1301 (1935).
Reduction of ethylene bromide to ethyl bromide over an alloy of Na and Zn.	Ethyl oxalate.	Michael: <i>J. Am. Chem. Soc.</i> , <b>25</b> , 419 (1901).
Reduction of benzaldehyde by Pt catalyst; suppressed by pure Pt.	FeCl <sub>3</sub> greatly accelerates reaction; Mn, Fe, and Ni salts, powerful oxidation catalysts.	Adams and Carothers: <i>J. Am. Chem. Soc.</i> , <b>45</b> , 1071 (1923); <b>46</b> , 1675 (1924); <b>47</b> , 1047 (1925).
Reduction of benzaldehyde to benzyl alcohol; reaction with finely divided Pt difficult; improved with Pt black; reduction with promoter proceeds beyond benzyl alcohol, continuing to toluene.	Smooth, uninterrupted reaction with increase in velocity in the presence of a trace of FeCl <sub>3</sub> or FeCl <sub>2</sub> .	Adams and Carothers: <i>Ibid.</i> , <b>45</b> , 1071 (1923); <b>46</b> , 1675 (1924). Willstätter and Waldschmidt-Leitz: <i>Ber.</i> , <b>54</b> , 113 (1921).
Reduction of aromatic nitro compounds by Cu catalyst.	Mg, Zn, or Fe oxides; 24.3 parts Cu carbonate and 2.7 parts Zn carbonate.	Sabatier and Senderens: (Badische Anilin u. Soda Fabrik): <i>Brit. P.</i> 13,149 (1914).
Reduction of nitrobenzene to aniline by Cu catalyst.	ZnO, Ag <sub>2</sub> O, or a mixture of MgO and Ag <sub>2</sub> O; 30 parts of CuO and 6 parts of ZnO.	Badische Anilin u. Soda Fabrik: <i>Brit. P.</i> 5,692 (1915).
Reduction of nitrobenzene (small insulation ability) + paraffin oil to aniline over Ni-kieselguhr.	Influence of high voltage discharge as promoter with increasing amount of the catalyst.	Seto and Ozaki: <i>J. Soc. Chem. Ind.</i> , <b>40</b> , 189B-191B (1937).
Reduction of aromatic hydrocarbons at ordinary temperature and pressure over Ni (prepared by reduction of the oxide at 200-300°).	3% Cr.	Truffault: <i>Bull. soc. chim.</i> , <b>1</b> , 206 (1934).
Reduction of citral to geraniol with PtO-Pt black catalyst and H <sub>2</sub> .	Fe sulfate or Zn acetate.	Adams and Garvey: <i>J. Am. Chem. Soc.</i> , <b>48</b> , 477 (1926).

Table 7. Promoters in Catalytic Hydrogenation and Dehydrogenation.

Reaction	Promoter	Observer
Hydrogenation of Na <sub>2</sub> SO <sub>4</sub> with Ni catalyst.	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .	Maxted: <i>Chem. Age</i> , <b>7</b> , 816 (1922).
Hydrogenation of CO and CO <sub>2</sub> , using Ni as a catalyst; CH <sub>4</sub> obtained.	Ce, Th, glucinum (Be), Cr oxides and silica increase reaction velocity 12 to 17 times; Zr, Mo and V oxides less active as promoters.	Medsforth: <i>J. Chem. Soc.</i> , <b>123</b> , 1452 (1923).
Hydrogenation of gases.	Mn stearates or resinsates accelerate oxidation.	G.P. 406,866, Kl 12o, November 29, 1924.
Hydrogenation of ethylene with NiH <sub>2</sub> catalyst.	Alcohol.	Weichselfelder: <i>Ber.</i> , <b>62</b> , 769-771 (1929).
Hydrogenation of alcohol with Cu catalyst.	MgCO <sub>3</sub> at 200°, so as not to decompose the carbonate completely; promoter acts differently on different surfaces.	Haggard: <i>J. Chem. Soc.</i> , <b>1932</b> , 2053-2062.

Table 7 (Continued).

Reaction	Promoter	Observer
Conversion of amylene into isopentane by CuO.	28 hrs. required in a Cu tube under 200 atm. pressure at 300°C.; 12 hrs. required in an Fe tube under the same conditions.	Ipatieff: <i>Ber.</i> , <b>43</b> , 3387 (1919).
Hydrogenation of galactose with Na amalgam.	Pb, Mn, and S.	Bertrand and Delancy-Auvray: <i>Bull. soc. chim.</i> , <b>53</b> , 1126-1129 (1933).
Hydrogenation of phenol with Ni catalyst.	Reaction accelerated to a greater extent by a mixed Cu catalyst than by Ni alone.	Dewar and Liebmann: <i>Brit. P.</i> 12,981 (1913); <i>Brit. P.</i> 15,668 (1914).
Hydrogenation of phenol vapor over a mixed Ni-alumina catalyst at 180°C.; in the presence of alumina alone, a temperature of 350°C. is required.	Ni-alumina.	Armstrong and Hilditch: "Catalytic Processes in Applied Chemistry," London.
Dehydration and reduction of cyclohexanol to cyclohexane.		
Hydrogenation of phenol with Ni catalyst.	Optimum effect with Na <sub>2</sub> CO <sub>3</sub> and 20-30% Ni; Na borate less active than Na phenolate, acetate, or sulfate.	Armstrong and Hilditch: <i>Brit. P.</i> 13,149 (1914).
Hydrogenation of phenol at Ni surfaces.	Na <sub>2</sub> CO <sub>3</sub> effectively promotes 25% by weight of Ni and appears to give maximum results.	Armstrong and Hilditch: <i>Proc. Roy. Soc. London (A)</i> , <b>102</b> , 21 (1922).
Hydrogenation of phenol under atmospheric pressure; catalysts prepared from heteropoly acids containing the activator as a central atom; general formulae: 1. Rn[x · (MoO <sub>4</sub> ) <sub>3</sub> ] x = P, Si, As, Th, Sn 2. Rn[M(MoO <sub>4</sub> ) <sub>3</sub> ] M = Cr, Ni, Co, Cu R = H, NH <sub>4</sub> , K	P, Ni, Cr, Si.	Kingman and Rideal: <i>Nature</i> , <b>137</b> , 529 (1936).
Hydrogenation of pinene and carvene with CuO.	Iron tube.	Ipatieff: <i>Ber.</i> , <b>43</b> , 3387 (1910).
Conversion of tetrahydrobenzene into hexahydrobenzene and tetrahydrotoluene into hexahydrotoluene with CuO.		
Conversion of camphor into camphane by reduction over Ni.	Mixed Ni-alumina catalyst; stepwise reactions carried out as one reaction at 200°C.	Ipatieff: <i>Ber.</i> , <b>45</b> , 3205 (1912).
Dehydrogenation of borneol to camphene over Al at 350°C. or above, and hydrogenation of camphene to isocamphane at 200°C.		
Hydrogenation of fenchone to fenchane with NiO catalyst at 240°; fenchol dehydrated to fenchene which is then hydrogenated to fenchane.	Fenchane obtained directly from fenchone at 215°C. by the addition of Al <sub>2</sub> O <sub>3</sub> to NiO.	Ipatieff: <i>J. Russ. phys. Chem. Soc.</i> , <b>44</b> , 1695 (1911); <i>Chem. Abs.</i> , <b>7</b> , 1170.
Hydrogenation of different hydrocarbons over Raney Ni.	Platinic chloride.	Lieber and Smith: <i>J. Am. Chem. Soc.</i> , <b>58</b> , 1417 (1936).
Hydrogenation of ketones and aldehydes over Raney Ni; the effect of promotion is not due to enolization, as in the case of benzophenone.	NaOH.	Delépine and Horeau: <i>Compt. rend.</i> , <b>201</b> , 1301 (1935). Delépine and Hanegraaff: <i>Compt. rend.</i> , <b>205</b> , 185 (1937).
Hydrogenation of aromatic compounds in alcoholic solution over Adams' catalyst.	HCl, HBr.	Brown, Durand and Marvel: <i>J. Am. Chem. Soc.</i> , <b>58</b> , 1594 (1936).
Hydrogenation of fluorene over Os catalyst.	Addition of 5% CeO <sub>2</sub> increases the activity of the catalyst almost eight times.	Sadikow and Mikhailov: <i>Ber.</i> , <b>61</b> , 1792-1806 (1928).

Table 7 (Continued).

Reaction	Promoter	Observer
Hydrogenation of fats with Ni catalyst.	Te.	Badische Anilin u. Soda Fabrik: G.P. 282,782 (1913).
Hydrogenation of fats.	Aniline accelerates the reaction.	Eymer: <i>Rev. Gen. des Mat. Colorantes</i> , <b>325</b> , 307-308, 352, 353 (1925).
Hydrogenation of cinnamic acid to cinnamyl alcohol without re-activation of PtO catalyst.	Zn and Fe salts.	Tuly and Adams: <i>J. Am. Chem. Soc.</i> , <b>47</b> , 306 (1925).
Hydrogenation of cotton-seed oil with Pt and Pd catalysts.	Mg.	Paal and Windisch: <i>Ber.</i> , <b>44</b> , 1013 (1911); <b>46</b> , 4010 (1913).
Hydrogenation of oils with Ni catalyst.	$\text{Ca}_3(\text{PO}_4)_2$ .	Bosch, Mittasch and Schneider: U.S.P. 1,215,335.
Hydrogenation of cotton-seed oil with Ni oxide.	Cu oxides; Ni oxide alone requires a temperature of about 250°C., while a mixture of Cu and Ni oxides reduce at 190°C.	Dewar and Liebmann: U.S.P. 1,268,692 and 1,275,405.
Hydrogenation of unsaturated oils.	X-rays, cathode rays and Mg salts.	Taylor: <i>J. Franklin Inst.</i> , <b>194</b> , 1-27 (1922).
Hydrogenation of maleic acid (benzaldehyde, methylethyl ketone, nitroguanidine, nitrobenzene) over Ni from a Ni-Al alloy (Raney's metal) at atmospheric pressure and room temp.; whether the catalyst is prepared from an alloy with 30% or 50% Ni does not matter. Alkali is a poison for the catalyst in reduction of nitrobenzene and other neutral substituted aromatic nitro-compounds (nitrotoluene, nitrophenetol); alkali, on the contrary, increases the velocity of reduction of methylethyl ketone, benzaldehyde and certain nitranilines and nitrophenols. o-Substituted aromatic nitro-compounds are reduced faster than the corresponding m-compounds and the latter faster than the p-compounds.	Chloroplatinic acid (added to the catalyst just before reduction).	Reasenbergl, Lieber and Smith: <i>J. Am. Chem. Soc.</i> , <b>61</b> , 384-87 (1939); refer also to Delépine and Horeau: (Refer to C. 1937 I 2953).
Dehydrogenation of $\text{CH}_3\text{OH}$ with Cu catalyst.	Th or Ce (no decrease in activity during 60 hrs.).	Ghosh and Bakshi: <i>J. Indian Chem. Soc.</i> , <b>3</b> , 415 (1926).
Dehydrogenation of $\text{HCHO}$ with Cu catalyst.	Ce.	Bakshi: <i>Ibid.</i> , <b>6</b> , 749 (1929).
Dehydrogenation of borneol to camphor with pure Ni catalyst (inactive).	A small amount NaOH or $\text{NaNO}_3$ .	Brit. P. 7,315 (1909).
Dehydrogenation of cyclohexane to benzene or methane over Ni and Co catalyst.	Ni-ZnO in any ratio; $\text{Ni-Al}_2\text{O}_3$ ; Al : Ni > 1 (Ni prepared by glowing freshly precipitated hydrated carbonate and reduction in excess of $\text{H}_2$ ). Co less active than Ni in dehydrogenation but more active in $\text{CH}_4$ formation; $\text{CaCO}_3$ or $\text{BaCO}_3$ (1%) increase catalytic activity of Ni; strongly increase the activity of Ni addition of Mn, Zn, Cr, Ce, Th, Al and Be oxides.	Juliard: <i>Bull. soc. chim Belg.</i> , <b>46</b> , 549-618 (1937)

Table 8. Promoters in Various Catalytic Reactions.

Reaction	Promoter	Observer
$\text{H}_2\text{O}_2 + 2\text{HI} \rightleftharpoons 2\text{H}_2\text{O} + \text{I}_2$ ; $\text{CuSO}_4$ , poor catalyst; $\text{FeSO}_4$ , good catalyst.	A mixture of $\text{CuSO}_4$ and $\text{FeSO}_4$ , more effective.	Brode: <i>Z. phys. Chem.</i> , <b>37</b> , 257 (1903). Traube: <i>Ber.</i> , <b>17</b> , 1062 (1884).
$\text{K}_2\text{S}_2\text{O}_8 + 2\text{KI} \rightleftharpoons 2\text{K}_2\text{SO}_4 + \text{I}_2$ $\text{CuSO}_4$ , catalyst.	A mixture of $\text{CuSO}_4$ and $\text{FeSO}_4$ , more effective.	Price: <i>Z. phys. Chem.</i> , <b>27</b> , 499 (1893).
Catalysis of $\text{NaOCl}$ .	Hydrates of $\text{MgO}$ and $\text{CuO}$ .	Lewis: <i>J. phys. Chem.</i> , <b>35</b> , 915 (1931).
Production of $\text{H}_2\text{SO}_4$ with V catalyst.	$\text{BaO}$ , more effective than $\text{CaO}$ .	Pincars: <i>Metallbörsc</i> , <b>22</b> , 625 (1932).
Volatilization of $\text{HCl}$ .	Accelerated by $\text{CuSO}_4$ ; only 1 mg. $\text{Cu}$ required for 100 cc. 1% $\text{NaCl}$ solution.	Bodner and Roth: <i>Z. anorg. Chem.</i> , 1101-1102 (1925).
Reaction between $\text{NH}_3$ and $\text{HCl}$ (no reaction when pure and dry).	Benzene causes an instantaneous reaction; it is assumed that benzene facilitates not only the formation, but also stabilizes colloidal $\text{NH}_4\text{Cl}$ which assists catalytically in uniting the $\text{HCl}$ and $\text{NH}_3$ molecules remaining; benzene functions as a <i>secondary catalyst</i> .	Kahlenberg: <i>J. phys. Chem.</i> , <b>6</b> , 1 (1902).
Corrosion of ferrous alloys and non-ferrous metals.	$\text{Ag-Cu}$ , promoter; $\text{Ni-Sn}$ , inhibitor; alkali carbonates cause metals to corrode more readily than does distilled water; according to the colloidal theory of corrosion, alkalies will act as inhibitors when used in a conc. sufficient to precipitate out the catalytic sol as rapidly as it is formed.	Friend: <i>J. Chem. Soc.</i> , <b>119</b> , 932 (1921).
$\text{Cu}$ catalyst for oxidation of $\text{NH}_3$ .	$\text{Pb}$ , or $\text{MnO}_2$ .	Badische Anilin u. Soda Fabrik: G.P. 301,362; <i>J. Soc. Chem. Ind.</i> , <b>40</b> , 794 (1921). Piggot: <i>J. Am. Chem. Soc.</i> , <b>43</b> , 2034 (1920).
Homogeneous catalysis of persulfate-iodide reaction.	$\text{Cu}$ and $\text{Fe}$ ions.	Kiss and Zonbary: <i>Rec. trav. chim. Pays-bas</i> , <b>46</b> , 225-239 (1927).
Formation of $\text{H}_2$ from $\text{CO}$ and steam, using oxides of $\text{Fe}$ , $\text{Ni}$ , or $\text{Co}$ as catalyst; source of $\text{CO}$ , water gas, which contains $\text{H}_2$ .	Admixture of $\text{Cr}$ , $\text{Th}$ , $\text{U}$ , $\text{Be}$ , or $\text{Sb}$ oxides in the proper proportions, i.e., 15% of the promoter.	Badische Anilin u. Soda Fabrik: E.P. 19,249 (1910); E.P. 27,963 (1913).
Reaction between $\text{CO}$ and $\text{H}_2\text{O}$ .	Reaction accelerated by the addition of alkali.	Taylor: <i>Proc. Int. Conf. Bit. Coal</i> , <b>1</b> , 190-199 (1928).
Reaction of coke with $\text{H}_2\text{O}$ .	Reaction accelerated by adding $\text{CaO}$ , $\text{Fe}_2\text{O}_3$ , or $\text{Na}_2\text{CO}_3$ to coke.	Taylor: <i>Ibid.</i> , <b>1</b> , 190-199 (1928).
Reduction of Schiff's bases with colloidal $\text{Pt}$ as catalyst.	Addition of $\text{NH}_3$ to catalyst induces a rapid adsorption of $\text{H}_2$ (no adsorption in a neutral solution in the formation of secondary bases).	Skita and Keil: <i>Ber.</i> , <b>61</b> , 1452-1459 (1928).
Reaction between mixtures of aldehydes and amines.	Amines accelerate the formation of secondary bases by increasing adsorption.	Skita and Keil: <i>Ber.</i> , <b>61</b> , 1452-1459 (1928).
Gas purification.	$\text{Fe}_2\text{O}_3$ .	Seil: E.P. 332,259, August 14, 1930.
Saponification of fats; hydrolysis takes place when 2-3% $\text{H}_2\text{SO}_4$ catalyst is heated up to $150^\circ$ ; in catalysis, stearosulfonic acid acts as a catalyst.	Benzene or naphthalene ring introduced into the compound to form benzene or naphthalene stearosulfonic acid; a more effective catalyst.	Twitchell.
$\text{C}_2\text{H}_4 + \text{Cl}_2$ ; $\text{C}_2\text{H}_4 + \text{Br}_2$ catalyzed by the glass walls of the reaction vessel.	Water.	Norrish: <i>J. Chem. Soc.</i> , <b>123</b> , 3006 (1923). Davies: <i>J. Am. Chem. Soc.</i> , <b>50</b> , 2769 (1928).

## POISONS

## Introduction

In catalytic reactions poisons are substances which interfere with the action of a catalyst by paralyzing or completely destroying its activity. Poisons show their full effect in minute amounts at very low concentrations with respect to the catalyst poisoned. The poisoning effect is most characteristic of heterogeneous systems. Poisons occur in the solid, liquid, and gaseous state. Among the solid catalyst poisons are lead, copper, manganese, cyanides, arsenates and unsaponifiable matter. Mercury, water, ethyl and amyl alcohols are among the liquid poisons, and carbon monoxide, carbon dioxide, hydrogen sulfide, sulfur, chlorine, oxygen, and water vapor act as gaseous poisons. These substances have been classified with respect to their action as: (a) violent poisons; (b) moderate poisons, and (c) feeble poisons.<sup>19, 20</sup>

## Types of Poisoning

In catalytic reactions, the poisoning effect varies, either as a function of time, or according to the type of poison. Thus poisoning may be permanent and irreversible, or temporary, disappearing on treatment with poison-free gases, because of displacement; it may be progressive, increasing with time, or, on the contrary, sudden; it may manifest itself as a so-called "fatigue" of the catalyst, the prototype of the poisoning effect, or it may be "selective," or general.

Tables 1, 2 and 3 show examples of various types of poisoning, including irreversible, temporary and progressive poisoning.

Table 1. Examples of Irreversible Poisoning.

Reaction	Poison	Observer
Synthesis of $\text{NH}_3$ over iron catalyst.	S compounds.	Watanaba: <i>Inst. Phys. Chem. Res. Tokyo</i> , 1, No. 10, 102 (1928).
Decomposition of CO over a catalyst.	S compounds.	Georg-Maria Schwab: Berlin, Verlag Julius Springer (1931).
Oxidation of $\text{NH}_3$ over Pt.	Acetylene; $\text{PH}_3$ (0.00002%).	Syrkin: <i>Zhur. Khim. Prom.</i> , 3, 1197 (1926).
Synthesis of $\text{NH}_3$ over uranium nitride.	Water vapor; a stable oxide is formed which has no catalytic activity.	Ussatschew: <i>Z. Elektr.</i> , 40, 647 (1934).
Oxidation of $\text{SO}_2$ over vanadium catalyst.	As; a compound is formed with the catalyst which is stable and inactive.	Adaduwow: <i>Trans. Mendeleew Congress Theor. Appl. Chem.</i> , 6th Congr., 2, 154 (1935).

The reasons for the "fatigue" of a catalyst are: (a) prolonged use of a catalyst in a reaction; (b) high temperature, causing the predominance of side reactions, so that highly condensed, slightly volatile, carbonaceous or tarry substances are slowly deposited on active surfaces, and (c) initial addition of substances, causing a partial poisoning. It is believed that the most active catalysts are most readily enfeebled in their action. In catalytic hydrogenations or decompositions by finely dispersed metals, the latter are very active and are readily induced into a state of fatigue.

Table 2. Examples of Temporary Poisoning.

Reaction	Poison	Observer
Catalysis of detonating gas mixture over Ni and Cu catalysts.	Oxide skin (abruptly diminishes the velocity of the reaction).	Benton and Emmet: <i>J. Am. Chem. Soc.</i> , <b>46</b> , 2728 (1924). Larson and Smith: <i>Ibid.</i> , <b>47</b> , 346 (1925).
Catalysis of detonating gas mixture over Ag and Au catalysts.	Oxygen; an increase in the activity of the catalyst is observed when oxygen is pumped off below the dissociation pressure of the oxide skin of the order 0.001 mm; Au oxide is unstable at atm. pressure and room temperature; the dissociation pressure of AgO is 100 times that of the pressure used at $10^{-4}$ mm.	Chapman, Ramsbottom and Trotman: <i>Proc. Roy. Soc., London (A)</i> , <b>107</b> , 92 (1925).
Decomposition of organic cpds. over a catalyst.	Deposition of sooty material caused a gradual loss in activity of the catalysts; initial activity readily restored by oxidation at relatively low temperature.	Zelinsky: <i>Ber.</i> , <b>59</b> , 156 (1926).
Detonating gas synthesis over Pt catalyst.	CO; a compound is formed between the poison and the catalyst; a non-catalyzing skin.	Georg-Maria Schwab: Berlin, Verlag Julius Springer (1931).
Decomposition of $\text{NH}_3$ over Fe catalyst.	$\text{O}_2$ .	Georg-Maria Schwab: Berlin, Verlag Julius Springer (1931).
Conversion of parahydrogen into orthohydrogen.	Ethylene, due to selective adsorption, poisons reversibly; ethane has a negligible effect.	Parkas and Rideal: <i>Proc. Roy. Soc., London (A)</i> , <b>146</b> , 630 (1934).
Oxidation of $\text{SO}_2$ over vanadium catalyst.	Vanadium sulfoxide; if the temperature is raised slightly above $400^\circ$ a sudden decrease in activity takes place; the inactive compound decomposes and the catalyst becomes active again.	Adadurow: <i>Trans. Mendeleev Congress Theor. Appl. Chem.</i> , 6th Congr., <b>2</b> , 154 (1935), refer also Boreskow: <i>Ibid.</i> ; p. 159.

Vavon and Husson<sup>139</sup> observed that platinum black capable of hydrogenating three compounds, A, B and C, was unable to hydrogenate A, but able to hydrogenate B and C with ease at a certain stage of fatigue; when a new factor causing fatigue of the catalyst was introduced, hydrogenation of A and B did not take place, but did take place for C. In the hydrogenation of limonene, Vavon and Husson were able to render plati-

Table 3. Examples of Progressive Poisoning.

Reaction	Poison	Observer
Hydrogenation of propylketone, piperonal, and nitrobenzene, applying colloidal Pt as catalyst.	$\text{CS}_2$ ; increasing addition of $\text{CS}_2$ suppresses the activity of the catalyst in the hydrogenation of piperonal, but not that of nitrobenzene; with a large amount of poison, the reaction with nitrobenzene ceases.	Vavon and Husson: <i>Compt. rend.</i> , <b>175</b> , 277 (1927).
Hydrogenation of nitrobenzene over Ni catalyst [prepared from $\text{Ni}(\text{NO}_3)_2$ ].	$\text{NiSO}_4$ causes progressive poisoning which is explained by the activity of single places in the active centers; the poison retards selectively the catalyzing power of the catalyst with respect to special reactions, such as hydrogenation of the benzene nucleus; 1.5-2 parts $\text{NiSO}_4$ to 100 parts $\text{Ni}(\text{NO}_3)_2$ limits the reduction of nitrobenzene to the formation of aniline and prevents the formation of cyclohexyl compounds.	Joshikawa: <i>Sci. Papers Inst. Phys. Chem. Res.</i> , (Tokyo), <b>24</b> , No. 513/23; <i>Bull. Inst. Phys. Chem. Res. (Tokyo)</i> , <b>13</b> , 54 (1934); <i>Sci. Papers Inst. Phys. Chem. Res. (Tokyo)</i> , <b>25</b> , 235-301 (1934).
Conversion of benzene to cyclohexane over Ni catalyst.	Thiophene poisons the catalyst to an extent depending on its partial pressure in the gaseous phase and not in proportion to the total amount of sulfur compound passed over the catalyst.	Roberti: <i>Gazz. chim. ital.</i> , <b>63</b> , 46 (1933).
Hydrogen electrodes in a mixed solution of KCl and HCl (0.001 or 0.1N conc.).	$\text{H}_2\text{S}$ (0.00025-0.00442N); the poisoning increases with increased concentration of $\text{H}_2\text{S}$ .	Mrs. Jablerynska-Ledziewska: <i>Roczniki Chemii</i> , <b>16</b> , 307-312 (1936).



num incapable of hydrogenating the double bond of the ring, but the double bond of the isopropenyl chain was readily hydrogenated.

Ginstling<sup>61a</sup> considers the fatigue of the  $\text{Fe}_2\text{O}_3$  catalyst used in the reaction  $\text{SO}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{SO}_3$  under 100 atmospheres and at high temperatures, and assumes that the reason for it lies in the conversion of a part of  $\text{Fe}_2\text{O}_3$  to  $\text{FeSO}_4$ . It is believed that a periodicity in the work would prevent fatigue, that is, application first of high pressure, then low, then high again.

"Selective" poisoning implies definite conditions, namely, (a) the rate of covering the catalyst with the poison varies with the nature of the active centers;<sup>40</sup> (b) the amount of poison sufficient to cover the catalyst must not be one molecule deep; (c) the poison itself must not possess any catalytic activity, and (d) during selective poisoning the centers of activity behave as if they constituted a surface of centers having the least heat of activation. Of course, poisoning may also be of a pure "mechanical" nature as has been demonstrated by Maxted<sup>90</sup> in the hydrogenation of liquid oleic acid in the presence of a suitable metallic catalyst at a temperature below the melting point of the product, stearic acid. The accumulation of the solid product on the surface of the catalyst prevented the access of fresh reactants (hydrogen) long before saturation of the oleic acid was attained. When the reaction temperature was raised above the melting point of stearic acid, no poisoning was observed. Sabatier and Senderens found the same mechanical poisoning effect produced by tarry products formed during hydrogenation of many organic compounds in the vapor phase. Likewise, oxide or carbon monoxide films formed over the catalyst during the process lowers its activity. For example, carbon monoxide film over platinum black surface lowers its activity considerably, as reported by Taylor and Burns.<sup>132</sup>

The division of the poisoning phenomena into types is not due solely to the formation of compounds between the catalyst and the poison, but depends on the degree of stability of the compound formed. This may be compared with the effect of a surface compound, as well as adsorption forces, which are especially strong for poisons, enabling them to displace the reactants from the catalyzing parts of the surface. Complete poisoning is not sharply defined; it is comparable to saturated adsorption.

### Evaluation of the Poisoning Effect

The poisoning effect may be evaluated by considering several characteristic factors. The first factor is the susceptibility of a given weight of a catalyst to a poison, which is termed the "poisoning coefficient," a function of the exposed effective surface of the catalyst and the fineness of its division. The activity of any poison expressed as a poisoning coefficient  $\alpha$  is given by the equation:  $K_c = K_o (1 - \alpha c)$ , where  $K_c$  is the reaction velocity constant in the presence of concentration  $c$  of the poison, and  $K_o$  the constant in the absence of the poison. The poisoning coefficient is independent of the components undergoing the catalytic reaction. This fact was observed for hydrogenation of nitrobenzene, acetophenone, benzene and oleic acid with mercury as a poison for platinum catalysts, and also in the case of hydrogenation of acetophenone and benzene in which carbon disulfide acted as a

poison. Poisoning in its early stages appeared to be equally effective on all parts of the active surface.

The second factor characteristic of the poisoning effect is its extent, *i.e.*, the absolute amount of poison necessary for complete inactivation of the catalyst. Ghosh and Bakshi<sup>81</sup> made an interesting tabulation of the amount required by various poisons to stop the reaction completely. In studying the dehydrogenation of methyl alcohol by a copper catalyst, these investigators recorded the behavior of carbon disulfide, chloroform, bromine and mercuric iodide. The results obtained are presented in Table 4.

Table 4.  
(Ghosh and Bakshi)

Poisons	Value of $K_1$ for Every Catalyst Used with Pure Methyl Alcohol	Total Catalyst (g. atoms)	Total Poisonous Substance (grams)	Total Poisonous Element in g. Atoms of S, Cl, Br and Hg	Total Poisonous Element in g. Atoms to Completely Poison 1 g. Atom of Catalyst
CS <sub>2</sub>	0.0267	0.12568	0.0329	0.000864	0.00687
CS <sub>2</sub>	0.0267	0.25136	0.0695	0.00182	0.00724
CHCl <sub>3</sub>	0.0253	0.12568	0.0326	0.000819	0.00651
Br <sub>2</sub>	0.0598	0.12568	0.01677	0.002009	0.01598
HgI <sub>2</sub>	0.0598	0.12568	0.01246	0.0000274	0.000218

This table indicates that doubling the quantity of the catalyst doubles the amount of poison required for complete poisoning to occur. Furthermore, using a catalyst of the same efficiency, the ratio of the number of gram atoms of poison (*e.g.*, sulfur or chlorine) to a gram atom of catalyst required for complete poisoning is about the same.

The third factor describing the poisoning effect is the tenacity with which a poison is retained at the surface of a catalyst, which is indicated by the so-called "retention factor." The latter is especially significant in connection with the problem of regeneration of poisoned catalysts. The degree of retention of a poison is related to its solubility and state of oxidation.<sup>112</sup> Pickles, studying the poisoning effect of carbon dioxide and carbon monoxide in the decomposition of hydrogen peroxide with platinum black as catalyst, found that although the absolute solubility of carbon monoxide is smaller than that of carbon dioxide yet, due to the slower rate of decrease in solubility with increasing temperature, it showed a greater poisoning effect on platinum black than that obtained for carbon dioxide (Table 5).

Table 5.  
(Pickles)

Solubility of CO/cc. of H <sub>2</sub> O Temp. (°C.)	CO/cc.	Solubility of CO <sub>2</sub> /cc. of H <sub>2</sub> O Temp. (°C.)	CO <sub>2</sub> /cc.
0	.035	0	1.71
10	.028	10	1.19
15	.025	15	1.02
20	.023	20	.88
30	.020	30	.66
40	.018	40	.53

On the other hand, although an arsenate is adsorbed to a greater extent by

iron hydroxide than an arsenite, the latter is retained with much greater tenacity.<sup>112</sup>

Maxted<sup>92b</sup> states that a certain rule is observed for the variation in the catalytic toxicity of a poison with its molecular structure, *i.e.*, the effective toxicity increases progressively with the molecular complexity of the normally non-toxic part of the poison. In the following table Maxted gives the relative toxicity per unit of sulfur with respect to a standard Pt catalyst in the catalytic hydrogenation of a series of alkyl sulfides and thiols.

Table 6. Relative Toxicity of Poisons (Maxted).

Poison	Mol. Wt.	Chain Length (A)	Relative Toxicity
Hydrogen sulfide.	34	—	1.0
Methyl sulfide.	62	2.58	7.1
Ethyl sulfide.	90	3.50	10.1
Butyl sulfide.	146	6.08	15.1
Octyl sulfide.	258	11.12	25.8
Cetyl sulfide.	482	21.20	34.1
Ethyl mercaptan.	62	3.50	3.9
Butyl mercaptan.	90	6.08	6.0
Octyl mercaptan.	146	11.12	10.1
Cetyl mercaptan.	258	21.20	13.1

The poison, by virtue of its negligible rate of evaporation, becomes attached permanently to at least one surface element by a linkage involving the poisonous element contained in its molecule. The permanent linkage at one point may cause the remaining, normally non-poisonous portion of the molecule to become effectively toxic. This Maxted calls the "anchor effect" in poisoning. As the length of the normally non-toxic chain increases, a lesser degree of effectiveness due to the recession of the anchor effect would be expected than for shorter chains. If this is correct, a second terminal sulfur atom at the opposite end of the chain would decrease the mobility, *i.e.*, restrict the surface potentially covered by an otherwise mobile chain of a given length, and consequently a decrease in molecular toxicity should be found. This has been confirmed.

Propylene dithiol ( $\text{SH} \cdot \text{CH}_2\text{CH}_2\text{CH}_2 \cdot \text{SH}$ ), in spite of the double sulfur content in comparison with the propylene monothiol  $\text{CH}_3\text{CH}_2\text{CH}_2 \cdot \text{SH}$  or *n*-butyl thiol  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \cdot \text{SH}$ , has been found considerably less toxic than the latter. It is believed that in this case two sulfur anchors are attached to the catalyst surface with the chain in a position of minimum strain. If the two sulfur anchors are adjacent to one another, instead of being at opposite ends of a hydrocarbon chain, then little effect on the toxicity is exerted by the second sulfur atom; for example  $(\text{C}_2\text{H}_5)_2\text{S}_2$ , in spite of double sulfur content, has the same molecular toxicity as  $(\text{C}_2\text{H}_5)_2\text{S}$ .

Recently Maxted and Evans<sup>92d</sup> studied the catalytic hydrogenation of crotonic acid in acetic acid by using as contact poisons  $\text{CN}'$ ,  $\text{H}_2\text{S}$ ,  $\text{AsH}_3$ ,  $(\text{CH}_3)_2\text{S}$ , and  $\text{Zn}''$ . The toxicity of these poisons with respect to a Pt catalyst was not considered as a function of the total amount of poison, but was related to the concentration of the poison actually adsorbed on the surface of the catalyst. The results obtained seem to indicate the existence of at least two types of active catalytic or adsorptive elements, in which those of one type are obviously equivalent among themselves.

### Effect of Poisons; Factors and Conditions Influencing Their Action

The main effect of poisons in catalytic reactions is the influence they exert upon the velocity of the reaction. Poisons may not only slow down a reaction, but stop it altogether. In rare cases there is a resemblance between the stimulating action exerted by poisons with respect to living organisms when taken in very small amounts and the accelerating effect exhibited in catalytic reactions. Chloroform and carbon disulfide, when taken in very small amounts, increase the velocity of dehydrogenation of methyl alcohol. Colloidal platinum, when used in the decomposition of hydrogen peroxide, is said (Bredig) to recover from carbon monoxide poisoning and to become more active than originally. The concentration of a poison apparently is indicative of the change in the velocity of catalytic reactions.

Ghosh and Bakshi,<sup>51</sup> studying the effect of poisons (carbon disulfide, chloroform, bromine, etc.) on the velocities of dehydrogenation of methyl alcohol with copper catalyst, stated that the decrease in the velocity constants of dehydrogenation is proportional to the amount of poison added. The velocity of the poisoned reaction is primarily a function of two factors, namely, temperature and time of contact. A study<sup>107</sup> of the decrease in the reaction velocity caused by poisons established the fact that the logarithm of the reaction velocity varies as a linear function of the contact time and thus, as poisoning progresses, the rapid initial rate of the decrease in the activity of the catalyst follows the simple law:<sup>40</sup>  $\log v = -kt + C$ . As the rate of poisoning of a reaction increases, the velocity may either remain constant or change, depending on the rate of temperature increase for the catalyst surface. Experimental results<sup>38</sup> on the rates of dehydrogenation of various alcohols, such as ethyl and amyl alcohols with copper as catalyst, showed that the temperature coefficient of the catalytic reaction remains unaltered after poisoning, except in special cases.

Kubokawa<sup>76c</sup> studied the decomposition of  $H_2O_2$  over Pt black (prepared either electrolytically or by reduction of the oxide) under successive addition of small amounts of mercuric ions as poison. Whereas Maxted<sup>92a</sup> assumed a linear relationship (for small amounts of poison) between the reaction velocity and the amount of adsorbed poisons, with a sharp break in the curve, whereby only two kinds of active centers could be available, Kubokawa found a linear relationship between the logarithm of the reaction velocity and the logarithm of the amount of poison, similar to the findings of Pease and Stewart<sup>110</sup> in a case of catalytic poisoning in an ethylene hydrogenation over copper with carbon monoxide. Kubokawa derives the energy distribution of active centers for platinum black from her experiments on the decreasing activity of the catalyst with progressive poisoning.

The influence of temperature upon poisoning has been emphasized in several instances. For example, it has been pointed out that there is relatively less irreversible poisoning with an increase in the temperature of the reaction.<sup>139</sup> The temperature coefficient in the decomposition of hydrogen peroxide by platinum black<sup>93</sup> is independent of the percentage of  $Hg^{++}$  ions

acting as a poison over the temperature range 0–25° and of a concentration of about 0.03 mg. mercury per mg. of platinum. In an investigation<sup>4</sup> of the poisoning of a vanadium pentoxide catalyst by arsenous oxide in the oxidation of sulfur dioxide, it was found that at 550° no poisoning takes place. The explanation given was that at this temperature other active centers than those poisoned by arsenous oxide cause the sulfur dioxide catalysis.

The poisoning effect<sup>138</sup> of gases, such as carbon monoxide, carbon dioxide, sulfur dioxide, nitrogen monoxide and nitric oxide, upon catalysts used in ammonia synthesis is less at higher temperatures (515°) than at lower temperatures (430°). Similarly, the poisoning of an iron catalyst promoted with aluminum oxide (1.3%) and potassium oxide (1.59%) in the synthesis

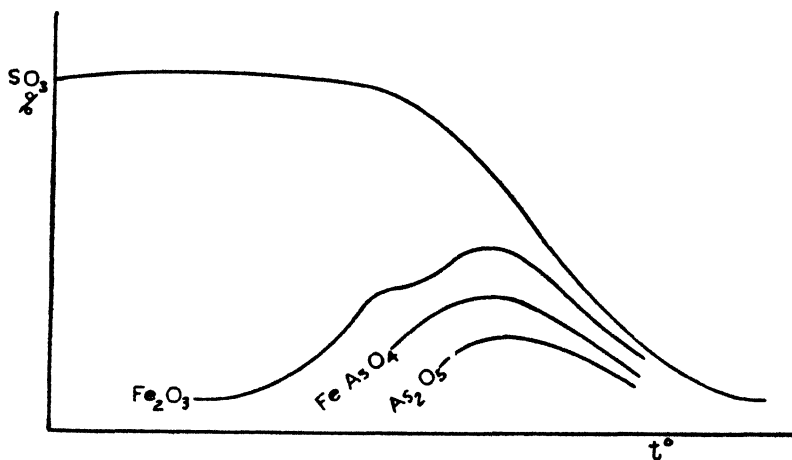


FIGURE 1.

of ammonia by hydrogen adsorption was found to be eight times greater at –78° for an equivalent amount of adsorbed hydrogen than at 100°. <sup>28</sup> Arsenic pentoxide (which is a poison in contact oxidation of sulfur dioxide to sulfur trioxide) acts as a catalyst giving a smaller yield at a higher optimum temperature. The yield for ferric oxide (625°) is 75 per cent; for ferric arsenate (650°), 63 per cent, and for arsenic pentoxide (675°), 50 per cent. Syrkin<sup>130</sup> has shown in Figure 1 that each of the indicated catalysts has a characteristic curve and that the actual poison in this case is water, from which sulfuric acid is formed.

Recently Burstein and Kashtanow,<sup>34</sup> investigating the para-ortho-hydrogen conversion over wood charcoal, found that the velocity constant at room temperature after adsorption of 0.2 cm hydrogen at 500° dropped one-thirtieth to one-fortieth of the value obtained for a pure carbon surface. At the temperature of liquid air it decreased only to one-third. A further increase in the adsorbed hydrogen activated at high temperatures influenced the conversion velocity considerably less. The rate of poisoning for a conversion at 300° was similar to that obtained at liquid air temperature. This has been explained by assuming that centers which are not

active at room temperature become active at 300° and at the temperature of liquid air. Centers active at room temperature are of the first order, while those active at 300° and at liquid air temperature are of the second order. The shape of the poisoning curves representing the velocity constants as a function of the amount of adsorbed hydrogen activated at high temperatures (calculated from the first order velocity equation) checks the above results. Measurements by static methods showed that the para-ortho-hydrogen conversion on charcoal at low temperatures (20–90°K.) has a positive temperature coefficient, and the apparent activation energy in this interval is 350 calories. With increasing temperature, the activity of both kinds of centers increases. Measurements by the dynamic method gave a positive temperature coefficient on pure charcoal at 90–573°K.; on poisoned charcoal (activated hydrogen adsorption), a negative temperature coefficient was obtained between 90 and 300°K. and a positive temperature coefficient for the interval 300 to 573°K.

Bork and Balandin,<sup>29</sup> in a series of papers on catalyst poisoning from the point of view of active centers, studied the kinetics of catalytic dehydrogenation of ethyl alcohol and *n*-propyl alcohol over copper and the influence of acetaldehyde and propyl aldehyde (poison), applying the following equation:  $dm/dt = K[(M - m)/N]$ ; where *m* is the number of moles of alcohol reacting and *M* the number of moles of alcohol entering the reaction chamber in unit time, and *N* is the total number of moles of gas in the reaction tube. The velocity of the catalytic reaction served to indicate the adsorbability of various molecules, thus accounting for the poison action. It was found that the retention of molecules of the alcohol and the aldehyde on the copper surface in the temperature interval 229 to 267° is the same in both instances and independent of the temperature. When the composition of the mixture in mol per cent was plotted against the corresponding velocity of hydrogen evolution, a straight line was obtained for the propyl alcohol-propionaldehyde, just as for the ethyl alcohol-acetaldehyde mixture. This indicates that the adsorption coefficients for the alcohol and for the aldehyde must be equal to each other, while the adsorption coefficient of hydrogen must be almost zero.

Plotting of the log *K* (velocity constant) against 1/*T* on the basis of measurements with 99.8 per cent propyl alcohol and ethyl alcohol at various temperatures for both alcohols gave the same activation energy, namely, *Q* = 12,800 cal./mol. The adsorption heats of ethyl alcohol and propyl alcohol and the corresponding aldehydes in this temperature interval were equally large. Thus, when dealing with two homologous substances which give the same dehydrogenation velocity according to Bork and Balandin, the activation energies must be equally large also. The adsorption coefficients of the second initial substance and of its dehydrogenation product should also become equal to each other if true for the first initial substance and its dehydrogenation product.

The pressure factor influencing catalytic processes under ordinary conditions also affects the adsorption of poisons. The variation in the efficiency of a catalyst with pressure is assumed to be different for each individual catalyst.<sup>6</sup> By passing from atmospheric to 100 atmospheres pressure, the

activity of the catalyst in some cases increased even more than under the influence of a promoter. In the synthesis of ammonia with promoted and unpromoted iron catalysts,<sup>45</sup> the poisoning action of water vapor at high pressure conformed with the rule—the higher the activity of the catalyst, the greater the amount of oxygen adsorbed—and much more oxygen was retained by the promoted than by the unpromoted iron catalyst. However, it was not certain whether the pressure or the promoter affected the adsorption of oxygen more. Under these conditions, the oxygen in the catalyst is considered to be present as an oxide and not as adsorbed molecules, the amount of oxygen being approximately proportional to the ratio of  $\sqrt{p\text{H}_2\text{O}}/\sqrt{p\text{H}_2}$  over the range of  $p\text{H}_2\text{O}$  and  $p\text{H}_2$  values used in the experiment, and not a function of the absolute value for  $p\text{H}_2\text{O}$ .

White and Benton,<sup>143</sup> studying the adsorption of hydrogen by nickel poisoned with carbon monoxide, expected from the work of others,<sup>55</sup> that only a gas adsorbed at very low pressures would be activated to an extent sufficient to cause catalytic reactions, and that carbon monoxide present in very small amounts would increase the adsorption of hydrogen at low pressures, tending to improve the activity of the metal rather than to poison it. However, these investigators found just the opposite of their expectations, namely, that hydrogen, although more readily adsorbed at 0° in the presence of carbon monoxide, is less active. This is due to the fact that the valence of hydrogen is largely saturated by the formation of a stable surface complex with carbon monoxide. The amount of hydrogen adsorption at all pressures up to one atmosphere at -183° was found to be decreased by an amount about equal to that of carbon monoxide used.

The function of poisons indicates that they are as influential a factor as the nature of the catalyst surface. The nature of a catalyst depends upon its source and method of preparation. Nickel catalyst, prepared in different ways, showed varying sensitivity toward poisons: nickel from basic nickel carbonate reduced in hydrogen at 450° was most susceptible to poisons; nickel from basic nickel carbonate reduced in hydrogen at 310° required larger amounts of poison; and nickel reduced at 450° on an inorganic carrier displayed unusual resistance to poisons.

Kelber<sup>71</sup> interpreted these results by explaining that heating the catalyst to a higher temperature produced a change in the surface so that only a few places on the particles composing it were able to adsorb and transfer the hydrogen. These particular points reacted more readily than the remainder of the catalyst and were the first to react with the poison, thereby poisoning the whole catalyst by comparatively small amounts of poison. Kelber's results are summarized in Table 6 which brings out the complexity of the function of poisons.

The poisoning effect differs also for catalysts with a high degree of molecular dispersion and those in a colloidal state. The greater the surface of the catalyst the more active it is. Poisoning of a catalyst in a colloidal state amounts to an agglomeration of colloidal particles so that the interfacial surface is changed considerably.

The specific susceptibility of certain groups of catalysts to various poisons may be a function of their adsorptive properties. It is a well known fact

Table 6a.  
(Kelber)

Catalyst	Temperature of Reduction °C.	Poison	Amount of Poison per g. Atom Catalyst	Hydrogenation Changes
(1) Ni from NiCO <sub>3</sub>	450	HCN	0.00005 0.0003	reduced to 45% inactive
(2) Ni from NiCO <sub>3</sub>	310	HCN	0.0003 0.001	reduced to 55% inactive
(3) Ni from NiCO <sub>3</sub> (on a carrier)	450	HCN	0.002 0.02	reduced to 25% inactive
(1) Ni from NiCO <sub>3</sub>	450	H <sub>2</sub> S	0.001 0.005	reduced to 75% inactive
(2) Ni from NiCO <sub>3</sub>	310	H <sub>2</sub> S	0.01 0.02	reduced to 15% inactive
(3) Ni from NiCO <sub>3</sub> (on a carrier)	450	H <sub>2</sub> S	0.02 0.1	reduced to 60% inactive
(1) Ni from NiCO <sub>3</sub>	450	CS <sub>2</sub>	0.0005 0.003	reduced to 25% inactive
(2) Ni from NiCO <sub>3</sub>	310	CS <sub>2</sub>	0.003 0.01	reduced to 60% inactive
(3) Ni from NiCO <sub>3</sub> (on a carrier)	450	CS <sub>2</sub>	0.01 0.06	reduced to 60% slightly active

that traces of poisons are very readily adsorbed by the catalyst, sometimes having a strong chemical action on it, the poisons causing the activity of the catalyst to fall rapidly.

Maxted<sup>89</sup> found that within certain limits the decrease in the activity of a catalyst is a linear function of the amount of poison. He investigated the influence of lead, mercury and arsenic poisons with respect to a platinum catalyst. The initial effect of additions of arsenic as illustrated in Figure 2 is considerably greater than that of the final amounts. Similar poisoning curves were obtained by Maxted and Lewis<sup>90</sup> for the decomposition of hydrogen peroxide and platinum black poisoned by mercury ions. By plotting the monomolecular reaction constant for this reaction against the concentration of the poison they obtained a curve similar to that shown below. The initial linear portion was believed to be due to that part of the adsorption isotherm for mercury on platinum which itself is linear. A subsequent increase in the concentration of mercury ions in the solution no longer gave a corresponding increase on the surface of the catalyst. Thus a linear relationship between the activity of the catalyst and the poison content is found up to a certain concentration of the poison; after which the slope of the curve is less steep and tends toward complete inactivity.

In all probability there are some individual methods for the preparation of catalysts which are stable toward specific poisons. A special method for the preparation of a catalyst is claimed<sup>108</sup> suitable for the conversion of water gas with water vapor at 320–330° and stable against such poisons as hydrogen sulfide.

Karschawin, Boguslawski and Smirnowa,<sup>70</sup> investigating the catalytic activity of nickel catalyst on chamotte as carrier for the complete conver-



sion of methane at  $1000^\circ$ , state that it does not lose its activity by passing 212,000 volumes of gas over one volume of the catalyst and that no poisoning effect of hydrogen sulfide is observed with 150–360 mg. sulfur per cc. in illuminating gas.

Adadurov and Grigorowitsch<sup>48</sup> studied the relationship between the decrease of activity and the change of lattice constants of catalysts in case of poisoning. The x-ray investigation of the influence of poisoning of Pt (Pt black) and  $\text{Cr}_2\text{O}_3$  catalysts through  $\text{As}_2\text{O}_3$  in the oxidation of  $\text{SO}_2$  showed that in both cases an increase took place in the lattice parameters (for Pt from  $a = 3.918$  to  $3.935 \text{ \AA}$ ; for  $\text{Cr}_2\text{O}_3$  from  $a = 4.940$  to  $4.955 \text{ \AA}$  and

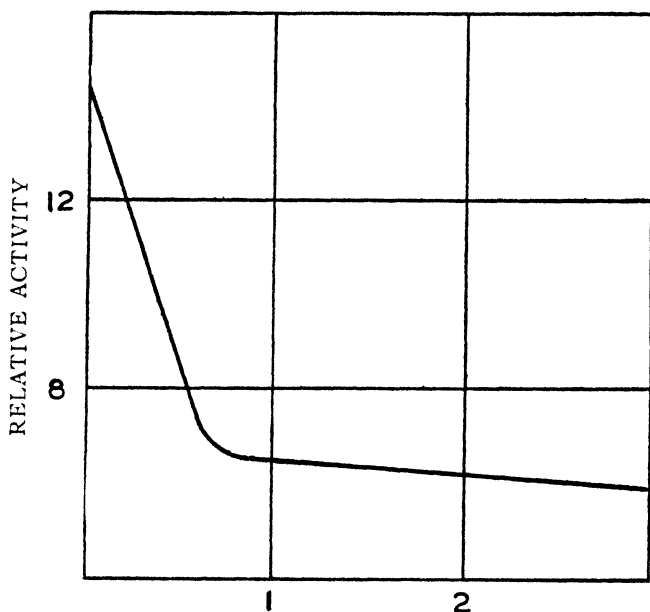


FIGURE 2.—Effect of Poison on 0.35 gr. Platinum.

for  $c = 13.58$  to  $13.65 \text{ \AA}$ ), without a change in the crystallographic system. According to these results, the change of the lattice constants for  $\text{Cr}_2\text{O}_3$ , and therefore the external field of the catalyst, by slow poisoning does not cause complete disappearance of activity, because after poisoning the catalyst will still cause a conversion of 50 per cent of the  $\text{SO}_2$  to  $\text{SO}_3$ . Platinum poisoning, up to 30 per cent, gave the same change in parameters as with a 50 per cent poisoning effect. Thus it has been assumed that not the total potential of the catalyst surface, but the form and field potential of active centers on the surface of the catalyst, is responsible for the catalytic action. This change must be so strong that the catalytic action is abolished. This actually occurred when Pt black was placed on Cu; in this case not only the lattice constant changed, but also the crystallographic form of Pt.

Poisons are specific for different catalysts, as well as for the different reactions in which they are employed. For example, hydrogen acts as a poison for water formation on iron-noble metal alloys, and oxygen poisons the water synthesis on nickel-noble metal alloys.<sup>118</sup> Water, in a high concentration, poisons carbon monoxide combustion with various catalysts.<sup>28</sup> Arsenic compounds are strong poisons for catalysts used in the contact process for the manufacture of sulfur trioxide. Arsenous oxide is a strong poison for catalytic hydrogenation with platinum due to its reduction to arsine. The same poison has relatively little effect upon the activity of platinum in the decomposition of hydrogen peroxide. Thus some substances may act as poisons for certain catalytic reactions and then again not at all; they may even act as promoters in other catalytic reactions. Bismuth, a strong poison for iron in catalytic hydrogenation, is one of the most active promoters for iron in the catalytic oxidation of ammonia to nitric oxide. Likewise, calcium phosphate is a promoter for nickel in catalytic hydrogenation, while phosphorus or phosphine is a strong poison. Nickel poisoned by thiophene does not hydrogenate the aromatic ring, while its ability to hydrogenate olefins is unimpaired.<sup>61, 78</sup> Sulfur or sulfides, which usually act as poisons in the catalytic reduction of benzoyl chloride and in the hydrogenation of tars, may themselves act as catalysts,<sup>92</sup> while carbon disulfide acts as an accelerator in the process of dissolving cadmium in hydrochloric acid solution.<sup>113</sup> There are cases in which a substance, when taken in small amounts, remains inactive, but when used in a large amount, acts as a poison. For example, in the reaction of naphthalene with a Japanese acid earth catalyst, chloroform is inactive in a small amount and does not have any poisoning effect, but when taken in a large amount it causes a decrease in the amount of resin formed with naphthalene under the influence of the earth. Hydrochloric acid when set free from chloroform and taken in large amounts decreases the catalytic activity.<sup>65</sup>

### Mechanism of Catalytic Poisoning

For the interpretation of the poisoning effect in its influence on catalytic reactions, several mechanisms have been proposed. Poisoning is primarily a "surface effect" as indicated by the fact that in the first stage the poisoning curve is related to the adsorption curve and that the activity becomes a linear function of the poison content. Bunsen,<sup>31</sup> in his day, perceived clearly that the removal of reaction products was essential to the continued action of a catalytic agent. Bodenstein and Fink<sup>25</sup> attributed the decrease in the reaction velocity to a decrease in the adsorption of reacting substances. In accordance with this explanation, poisons may function in preventing the adsorption of reacting compounds by being adsorbed themselves instead. Meyerhof,<sup>96</sup> studying the influence of narcotics upon the hydrogen peroxide decomposition with colloidal platinum, assumed that an isolated layer of the narcotic forms around the platinum particles which prevents the contact of the reacting substance with the catalyst.

Boeseken and Weide,<sup>26</sup> investigating the kinetics of reduction of unsaturated organic compounds in the presence of colloidal platinum and palladium, believed the process to be caused by diffusion of hydrogen and

the substance to be reduced through a layer surrounding the catalyst. If this layer could not be penetrated by the reacting components of the system, it was inferred that poisoning took place.

Bancroft<sup>19, 21</sup> pointed out the significance of adsorption in poisoning phenomena. Contact catalysis is slowed down if a poison is readily adsorbed, thus interfering with the normal adsorption of the reactants on the catalyst by preventing them from reaching the surface. He pointed out later<sup>22</sup> that catalytic poisoning owed its effect to a marked "selective" adsorption. This statement was supported by experimental evidence<sup>116</sup> showing that carbon monoxide, when added in small amounts to platinized asbestos with adsorbed hydrogen, was able to displace the adsorbed hydrogen from platinum in certain catalytic hydrogenations. The adsorption coefficient for platinized asbestos was found to be greater than that of platinum black, indicating that platinized asbestos has a greater specific surface than platinum black.

Wolff<sup>144</sup> viewed poisoning as not being exclusively based upon adsorption. Adsorption would be the most significant factor in the interpretation of catalytic poisoning if the poisons were present in an amount large enough to enable the entire surface of the catalyst, or the greater part of it, to adsorb the poison. But in ordinary catalytic poisoning the poisonous substance shows its full effect at very low concentrations.

Vavon and Husson<sup>139</sup> considered poisoning of a catalyst, which is a hindrance to the reaction, to be based on a preferential adsorption of the poison on active points of the surface with the result they are not capable of producing a proper deformation of the reactants. The theory<sup>39, 72</sup> that some groups of atoms "centers of activity," which normally are more active than others, are preferentially poisoned has likewise been applied in interpreting the mechanism of the poison action.

Although the difficulty of hydrogenation in the series of crotonic acid, oleic acid and benzoic acid increases from left to right, Maxted and Stone<sup>93c, 93d</sup> found that the amount of poison required for decrease in activity of a standard Pt catalyst to a definite fraction of its initial value (in the poison-free catalyst) has the same value in each case, instead of changing stepwise as was the case in Vavon and Husson's experiment.<sup>139</sup> The writers found that the poisoning coefficient  $\alpha$  has about the same value for the reaction velocity  $K_c$  for all cases, whence the following relationship was established:  $C : K_c = K_o (1 - \alpha)$ . This is considered as a support for assuming the homogeneity or equal valence of catalyzed places on the metallic surface, and for the participation of the same parts in all the reactions investigated. This is in agreement with the Schwab-Pietsch hypothesis<sup>126a</sup> rather than with the conception of the existence of special lattice elements of various kinds as places at which catalysis takes place.

The poisoning of a catalyst has been considered by Bork and Darykina<sup>29a, 29b</sup> from the view point of the specificity of active centers. A special method was used for quantitative determination of the relative time of stay of water molecules and alcohol molecules on Cu catalyst in the catalytic dehydrogenation of alcohol. The water did not participate in the reaction, and the protective action exerted by it was based on partial re-

removal of the aldehyde from the catalyst surface through dehydrogenation of the aldehyde hydrate formed to acetic acid, which took place at 250°. The ratio of time of stay of water molecules to that of alcohol molecules at 257.5° was determined as equal to 0.250.

The idea of inequality in the catalytic efficiency of surface atoms<sup>11, 48</sup> originated from the fact that small amounts of poisons suppress the activity of comparatively large surfaces of reduced metal catalysts. The above fact suggested to many investigators the thought that relatively small parts of the metal catalyst are active in the catalytic process.

By experimenting with arsenous oxide poison<sup>3</sup> in the catalytic oxidation of sulfur dioxide with vanadium catalysts, it was found that poisoning causes a decrease in the number of catalytically active centers at a given temperature. On the other hand, a study of the effect of nitrogen and iron on the catalytic behavior of charcoal in the oxidation of oxalic acid<sup>120</sup> showed that all poisons, as a rule, are not necessarily preferentially adsorbed on the most active catalytic areas. The curve obtained by poisoning this catalyst with potassium cyanide was of a different nature from that obtained with iron-containing charcoal free from nitrogen. Amyl alcohol differentiated catalytically between active and inactive carbon, the life span of the poisoning alcohol molecules on the active carbon being greater than that of oxalic acid on the active carbon. However, potassium cyanide and potassium thiocyanate were more readily adsorbed on an iron-carbon surface than on an iron-carbon-nitrogen surface, although the latter is catalytically more active; but the difference in the life span of the cyanide ion on the iron-carbon surface and iron-carbon-nitrogen surface was not as great as that of the thiocyanate ion which, therefore, must be considered as a more selective poison. The residual affinity of iron-carbon complex for cyanide and thiocyanates is greater than that of the iron-carbon-nitrogen complex. The catalytic activity for the oxidation of oxalic acid is much less.

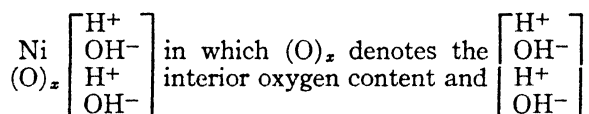
Although the poisoned state has been described as one in which poisons decrease the free association of the catalyst with the reacting components by replacing them, an exception to this rule has been introduced by Ishimura.<sup>66</sup> His investigations seem to indicate that only strong poisons act by reducing the catalytic activity through a selective and strong adsorption on active centers which they convert to an inactive state. However in the case of weak poisons relatively large amounts of them must be retained and even when all of the active centers are covered by the poison, they are readily set free in the course of the reaction.

A slightly different explanation for the loss of the ability of the catalyst to adsorb the reacting components is that the poison saturates a number of secondary valence bonds, rendering them inactive for normal catalysis.<sup>89</sup>

If poisoning is initiated by the adsorption of poisonous substances, such as gases, the reason for the effect may be sought in a destruction of something vital to catalysis. The experimental results of McLaughlin<sup>94</sup> showed that a normal platinum or nickel catalyst consists of metal particles with an interior oxygen content and that these metal particles are surrounded by an external layer of dissociated water (hydrogen and hydroxyl ions), which is the actual seat of catalytic reactions, such as oxidation, reduction,

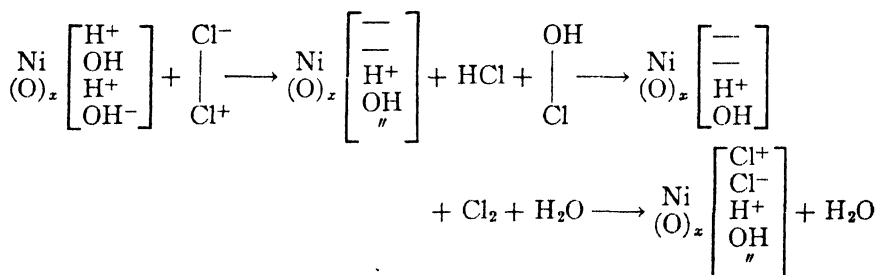
or hydrolysis with platinum black or reduced nickel oxide as catalyst. These external layers or films protect the underlying interior oxygen content.

Boswell and Bayley,<sup>30</sup> in their study of the poisoning effect of nickel and platinum catalysts by chlorine, believed that the poisoning is carried out by the destruction of the surface film which is the seat of the catalytic action. This destruction renders the interior oxygen content of the catalytic complex, which is necessary for the maintenance of the film, accessible to free hydrogen. The oxygen contained in the catalyst is active when it is free and able to associate with hydrogen, and inactive when it is protected. Small quantities of poisons remove the protection whereby the inactive oxygen is made reactive. The poisoning of a nickel catalyst made up of a number of nickel atoms (the number of which is a function of fineness of division, conditions of preparation, etc.) by chlorine poison was illustrated by Boswell and Bayley as follows:

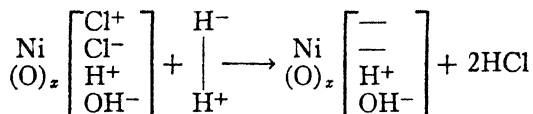


expresses the film.

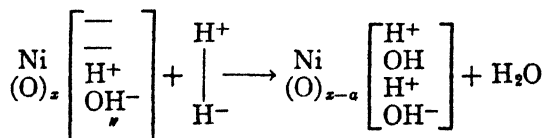
When chlorine poison acts upon the catalyst, an equivalent amount of water is evolved, passing through the following stages:



Introduction of hydrogen into the system causes primarily a partial removal of the surface layer, resulting in the formation of free water.

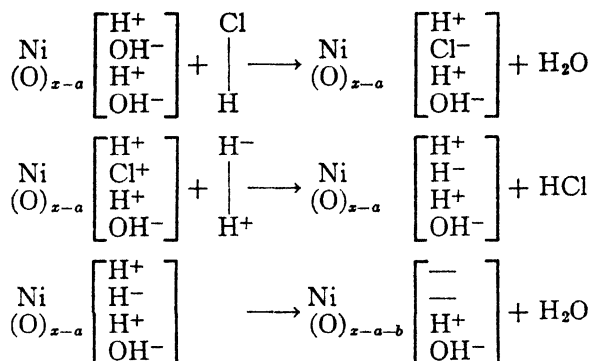


Later, there is a tendency to re-establish the original surface film.



When the rate of action of hydrochloric acid destroying the surface film predominates over the rate of restoration of the film by the action of free

hydrogen on the interior oxygen, then the surface film is quickly destroyed and a relatively large amount of water is liberated followed by an adsorption of the evolved hydrochloric acid. This cycle is assumed to be continuous, and may be illustrated as follows:



Thus, in brief, the action of chlorine poison is accompanied by the evolution of an equivalent amount of water but, on the other hand, the tendency to re-establish the original surface film does not cease and, in order that poisoning may take place, the rate of action of the poison must predominate over the rate of restoration of the surface film.

In considering the mechanism of the poison action, it should not be forgotten that certain poisons may have a tendency to spread themselves out as obstructive films on the surface of the catalyst while others may penetrate the catalyst mass involving thereby diffusion and occlusion.

Taylor and Burns<sup>132</sup> considered the poisoning effect in heterogeneous catalysis to be due to an obstructive film, the quantity of poison necessary to form it being relatively small, and its removal possible by converting it into a form less readily adsorbed. These investigators emphasized the fact that the obstructive film may be adsorbed on the surface of the catalyst with or without penetration of the poison into the mass of the catalyst, thus implying, the possibility not only of adsorption, but of diffusion as well.

In this case the cause of the poisoning effect may be attributed to: (a) the destruction of the heterogeneity of the catalyst surface by converting the active points into a plane crystal face, *e.g.*, small quantities of mercury vapor produce complete poisoning, and it is considered more poisonous with respect to copper catalyst<sup>51</sup> than carbon disulfide or chloroform, because of the manner in which the mercury vapor condenses on an active point, dissolves it, and spreads it out into a smooth thin layer; this action is repeated in quick succession for all the points involved; (b) the fact that gaseous poisons surround the colliding molecules which induce the catalytic reaction, orienting them in such a way that poles unsuitable for the reaction are turned towards one another.<sup>117</sup> This orientation theory postulates that a single layer of poison may suffice in stopping a catalytic reaction, and less than a single layer may reduce its rate a few hundred or even a thousand times. The mechanism of poisoning in such a case may be referred to as a paralysis of the forces acting between the reacting components, and this

interpretation is in agreement with the fact that the first traces of a poison sometimes lower the rate of the reaction, while subsequent increase in the amount has no apparent effect. For example, this is the case of the poisoning effect of carbon monoxide in the decomposition of ammonia with copper as catalyst.<sup>13</sup> For this particular case, Taylor<sup>135</sup> showed that carbon monoxide has a higher heat of adsorption on copper than hydrogen and ammonia; small traces of carbon monoxide can therefore poison the reaction.

The mechanism of the poison action has been presumed to be not only physical and related to a decreasing ability of the catalyst to adsorb or to occlude gases, such as hydrogen, and to a lowering of its partial pressure on the catalyst, but may be chemical if the poisons react with the catalyst. Thomas,<sup>137</sup> in his investigation of the poisoning effect of nitrogen, carbon monoxide and hydrogen sulfide in hydrogenations, believed that each of these poisons is typical of its class. Nitrogen, which had been assumed to act solely as a diluent (although the effect was considered somewhat greater) was proved by him to be typical of gases which undergo no chemical action with or under the influence of a catalyst. Therefore, the poisoning action of nitrogen was considered by Thomas as physical. The action of carbon monoxide was assumed as typical of gases which undergo reaction with hydrogen in the presence of a catalyst. The poisoning effect of this group of poisons is much greater than that of the first, and they not only diminish the adsorptive power of hydrogen by the catalyst, but may occlude and even dissolve in the catalyst, absorbing some of the energy emitted by it, and themselves becoming reactive. Hydrogen sulfide, a member of a third group, was shown to be typical of gases which react with the catalyst itself, forming stable compounds at temperatures of the experiment.

Bach<sup>14</sup> investigated the poisoning of palladium catalysts used in the reaction:  $\text{NaH}_2\text{PO}_2 + \text{H}_2\text{O} \longrightarrow \text{NaH}_2\text{PO}_3 + \text{H}_2$  and found that the poison acted partly by a chemical combination with palladious chloride and partly by adsorption on palladium black.

White and Benton<sup>143</sup> concluded from their experiments on the adsorption of hydrogen by nickel poisoned with carbon monoxide that poisons do not prevent the adsorption of hydrogen on the active areas of the catalyst, but do form a surface compound with hydrogen molecules.

Girard and Dreyfus<sup>52</sup> favored the idea of intermediate compound formation between the catalyst and poisons like sulfur, phosphorus, arsenic, or halide compounds. They succeeded in reactivating the poisoned metal by dissociation of the intermediate compounds through the introduction of an electromagnetic field.

Kubota and Jamanaka<sup>76</sup> attempted to illustrate the poisoning effect, basing their model (Fig. 3) on Balandin's conception regarding the activity of a multiplet.

Figure 3 shows how, according to this theory, the activity of a multiplet is weakened or even entirely lost under the poisoning action of thiophene by an increase in the distance between the active centers of the reactants. In this figure, *A* is the nickel atom which is the adsorption center of the methane molecule; *R*<sub>1</sub>, *R*<sub>2</sub>, and *R*<sub>3</sub> (nickel atoms) are the reaction centers

attracting hydrogen molecules, and  $P$ , the adsorption center of the water molecule  $w$  (a metallic oxide promoter). The catalytic reaction for which

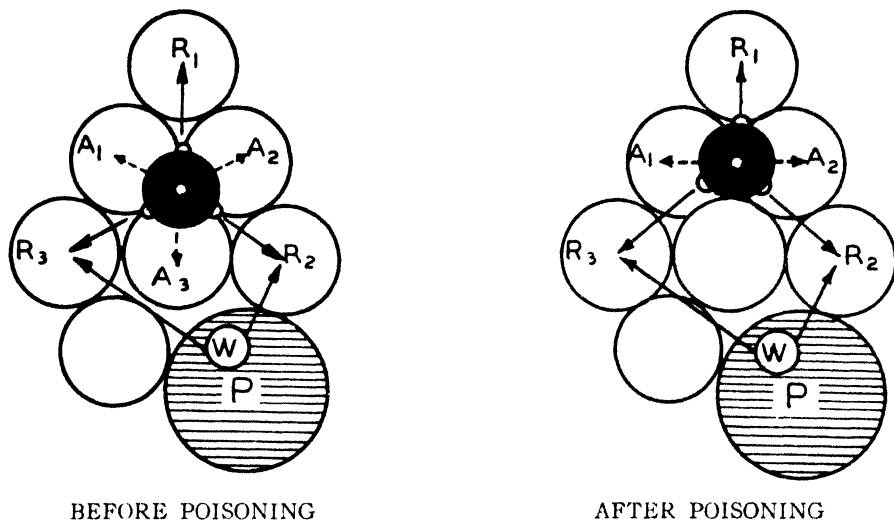
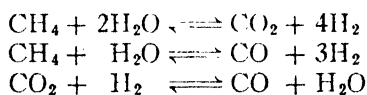


FIGURE 3.

the poisoning effect is illustrated is the catalytic oxidation of methane with steam, using nickel as a catalyst:



When the nickel catalyst was promoted with aluminum oxide, the ratio of the products was  $\frac{\text{CO}_2}{\text{CO}} = 49.0$  (at  $1000^\circ$ ); when it was subjected to the action of thiophene, the ratio was  $\frac{\text{CO}_2}{\text{CO}} = 1.02$  (at  $1000^\circ$ ).

### Characteristics of Individual Poisons

#### 1. Carbon Monoxide

The poisoning action of carbon monoxide on various metal catalysts has been known for a long time<sup>59</sup>. DeHemptinne<sup>42</sup> found that palladium treated with carbon monoxide no longer adsorbed hydrogen. Paal and Hartmann,<sup>104</sup> studying catalytic hydrogenation, observed the inhibition of the activity of palladium catalyst by carbon monoxide. Thomas<sup>137</sup> stated that the poisoning effect of carbon monoxide is considerably greater than that of nitrogen. Taylor and Burns<sup>132</sup> showed the tenacity with which carbon monoxide as a typical obstructive film is held by platinum black, the amount of carbon monoxide poison forming the obstructive film being relatively small. Experimental investigations<sup>19, 21</sup> have shown that platinum, which holds carbon monoxide tenaciously, is not a good catalytic agent for



the reduction of carbon monoxide to methane, whereas this reaction proceeds readily with palladium from which carbon monoxide may be removed with ease by hydrogen at ordinary temperature.

Pickles,<sup>112</sup> studying the poisoning effect of carbon monoxide, carbon dioxide, and a mixture of the two on the decomposition of hydrogen peroxide in the presence of platinum black, found that carbon monoxide had a considerably greater poisoning effect than carbon dioxide, the effect of carbon dioxide being small, and decreasing with an increase in temperature. Pease and Stewart<sup>110</sup> found that a minute amount of carbon monoxide reduced the activity of a copper catalyst in an ethylene-hydrogen reaction by 88 per cent. In studying the effect of small amounts of carbon monoxide on the adsorption of hydrogen and ethylene by copper, Griffin<sup>55</sup> found that a very small amount of the poison increased the adsorption of hydrogen. Since it is difficult to visualize a few molecules of carbon monoxide alone attracting and holding hydrogen molecules greater in number, it was assumed that carbon monoxide changes the surface activity of the catalyst so as to make available more areas for the adsorption of hydrogen. Three possibilities have been suggested for this increase in hydrogen adsorption: (a) carbon monoxide increases the activity of the most active areas; (b) carbon monoxide stimulates the inactive areas, and (c) carbon monoxide creates entirely new areas. Since carbon monoxide is adsorbed on the most active areas, the first postulate regarding the increase in activity appears to be acceptable. With a copper catalyst, the increase in hydrogen adsorption is noted only at low pressures, for the poisoned isotherm crosses the pure hydrogen isotherm at relatively low pressures. With a nickel catalyst,<sup>51</sup> the increase in hydrogen adsorption is observed at all pressures up to one atmosphere, even when very small amounts of carbon monoxide are used. Kistiakowsky, Flosdorf and Taylor<sup>72</sup> interpreted the decrease of hydrogen activity at higher pressures on copper poisoned with carbon monoxide by assuming that the process of sorption includes a second factor, such as dissociation, in addition to surface adsorption. A very small amount of carbon monoxide is sufficient to prevent the dissociation of hydrogen in copper by making the active centers on copper inactive.

The adsorption of one gas may be reduced by the presence of another, more strongly adsorbed gas. However, the catalytic activity often is reduced to a far greater extent than the adsorption. In a hydrogen-ethylene reaction catalyzed by finely dispersed copper, a trace of mercury reduces the rate of the reaction 200 times, while the adsorption of ethylene is reduced by 14 per cent and that of hydrogen by 80 per cent.<sup>111</sup> It is therefore assumed that there are two kinds of adsorptive areas, one on which the poison (mercury) is adsorbed to the exclusion of hydrogen, and the second on which ethylene is adsorbed. The main seat of catalytic action is occupied by mercury. Griffin<sup>55</sup> obtained isotherms for the adsorption of hydrogen on finely dispersed copper at 0° in the presence of carbon monoxide and cyanogen, and also for these gases separately (Fig. 3a). The cyanogen is very strongly adsorbed and behaves like mercury; it reduces the adsorption at all pressures. Carbon monoxide, on the other hand, produces a slight increase in adsorption at low pressures.

Benton and White<sup>143</sup> have found that carbon monoxide affects the adsorption of hydrogen by nickel in such a manner that a much smaller amount of CO is necessary to inhibit the reaction than is required for the formation of a mono-molecular layer. CO is also so strongly adsorbed that it cannot be completely pumped away at 200°.

Epstein and Upolownikow,<sup>46a</sup> studying the activity of Ti magnetite and Fe catalysts in ammonia synthesis, poisoning the  $N_2$ - $H_2$  mixture with 0.01–0.1 per cent by volume of  $O_2$  or 0.02–0.1 per cent by volume of CO, ascertained that the first amounts of poison cause a considerable decrease in activity, which gradually disappears. This is interpreted in the sense that the most active places of the catalyst are bound only in a reversible process.

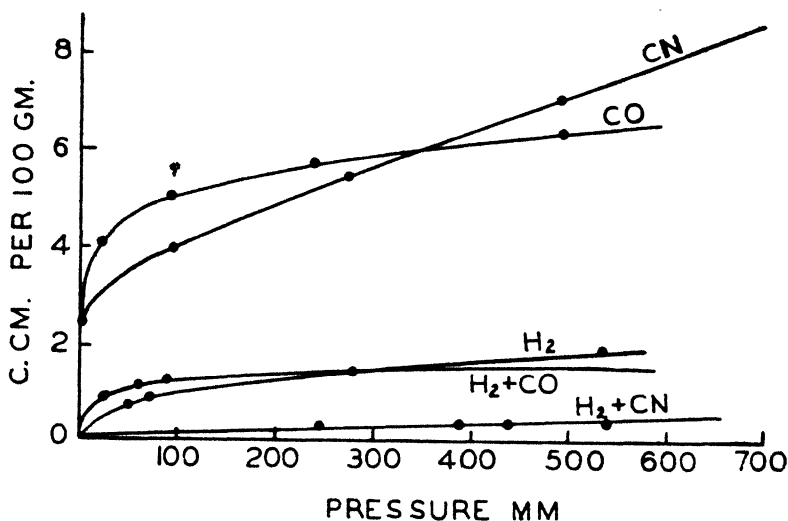


FIGURE 3a.

Further the activity is retarded more strongly if the concentration of the poison (C-vol. %) increases. It is assumed that the following relationship holds between  $C$  and the activity decrease  $\Delta y$ , expressed as retrogression of the per cent approximation to the equilibrium:  $C/\Delta y = KC + b$ , where  $K$  and  $b$  are constants (the attained concentration of  $NH_3$  is applied directly as a scale for the action).

Sieverts<sup>128</sup> believed that a small amount of hydrogen is soluble in nickel, while White and Benton<sup>143</sup> maintained that there is no solubility of hydrogen with or without the presence of carbon monoxide. They assumed that either the carbon monoxide increases the hydrogen adsorbing areas by the amount of carbon monoxide present in each case, or the hydrogen is adsorbed on top of the carbon monoxide as a secondary layer.

White and Benton compared the inhibiting action of carbon monoxide towards the adsorption of hydrogen by nickel with the action of drugs which have an optimum dose for stimulating body activity, but which produce death when administered in large amounts. When an amount

equivalent to 0.04 cc. produces a maximum increase in the hydrogen adsorption, 1.00 cc. causes a decrease in the previous adsorption value, and larger amounts of carbon monoxide decrease the adsorption value still further.

Watanabe<sup>141</sup> reported an unusual result which he observed while studying the poisoning effect of certain substances on iron catalyst in the decomposition of carbon monoxide, namely, that the efficiency of its decomposition was gradually decreased by the addition of naphthalene. After 5 hours, only 38 per cent of the initial value was obtained. The passage of pure carbon monoxide for 2 hours had a negligible effect on the poisoning. Watanabe interpreted this phenomena as the result of the condensation of naphthalene on the surface of the catalyzer, with a consequent retardation of the reaction.

Taylor<sup>135</sup> showed that carbon monoxide has a higher heat of adsorption on copper than hydrogen or ammonia and that therefore small traces of carbon monoxide poison the decomposition of ammonia. Dixon,<sup>43</sup> studying the poisoning effect of carbon monoxide upon the decomposition of ammonia with copper as catalyst, found that the first trace of carbon monoxide lowered the rate of decomposition appreciably, but a subsequent increase in the amount had no apparent effect. The behavior of carbon monoxide was described as follows: A very small partial pressure of carbon monoxide is sufficient to cover the few active patches on the catalyst, a further increase in its pressure making it unnecessary for carbon monoxide to compete for a portion of the uniform copper surface; therefore, the effect of additional carbon monoxide is similar to that of dilution with hydrogen.

Table 7. Action of Carbon Monoxide upon the Decomposition of Ammonia with Copper Catalyst.

Ammonia (cc./min.)	Carbon Monoxide (cc./min.)	Ammonia Decomposed (%)
32.3	0.00	21.60
32.3	0.30	18.00
32.3	0.79	18.20
32.3	1.34	18.00
43.8	0.00	18.40
43.8	0.35	15.65
43.8	0.70	15.40
43.8	1.20	14.85
43.8	1.35	14.85

$t = 581.5^\circ$

Siebert<sup>127a, 127b</sup> studied the influence of carbon monoxide poison upon the yield in the oxidation of  $\text{SO}_2$  by air.

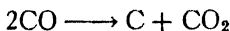
Table 8.

(Siebert)

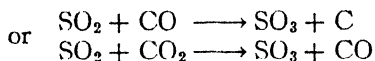
	Temperature (°C.)	Yield $\text{SO}_3$ (%)	Time
5% $\text{SO}_2$ + 95% air	410-505	97-98	
5% $\text{SO}_2$ + 95% air + 5% CO	435	83	after 26 hrs.

An electrically heated K-V catalyst on kieselguhr was used, and it is assumed that the decrease in yield may be attributed to the formation of

S and COS from  $\text{SO}_2$  or  $\text{SO}_3$  and CO, which hinders the process by displacing the equilibrium. CO decomposes according to:



and reactions such as



may take place.

## 2. Hydrogen Sulfide and Sulfur Compounds

Maxted<sup>89</sup> showed that hydrogen sulfide not only inhibits the catalytic activity of palladium, but also influences the occlusion of hydrogen. He studied quantitatively the relation between the occlusion power and the poison content, finding that the depression in the occlusion power of palladium for hydrogen was a linear function of the sulfur content in the catalyst. The hydrogen sulfide adsorbed quantitatively by palladium dissociated into sulfur and hydrogen. The relationship between the sulfur content<sup>89</sup> and the activity of a platinum catalyst in the hydrogenation of oleic acid was linear up to a certain concentration of the poison; beyond this point the poisoning curve slopes less toward complete inactivity.

Yablezynska-Jedrzejska and Domanski<sup>146, 147</sup> studied the poisoning of the  $\text{H}_2$  electrodes by  $\text{H}_2\text{S}$ . The velocity of poisoning by  $\text{H}_2\text{S}$  is the smaller the thicker the layer of the Pt black on the electrode. In a fresh  $\text{PtCl}_4$  solution the  $\text{H}_2$  potential is lower than in an aged  $\text{PtCl}_4$  solution. The poisoning with  $\text{HCl}$ ,  $\text{HBr}$  and  $\text{H}_2\text{SO}_4$  follows in about the same way under a sudden increase of the potential; the effect of  $\text{H}_3\text{PO}_4$  is slightly weaker. The velocity of poisoning with  $\text{H}_2\text{S}$  always increases with increasing concentration of  $\text{H}_2\text{S}$ .

The sudden rise in the potential after the first addition of  $\text{H}_2\text{S}$  is considered as an increase of the negative charge on the electrode, because of the decrease in  $\text{H}'$  concentration due to the reaction:  $\text{H}_2\text{S} + \text{H}' \longrightarrow \text{H}_3\text{S}'$ ; the change is obviously only in few millivolts.

The writers assume that through adsorption on the electrode the ionization of  $\text{H}_2\text{S}$  is increased and thereby the  $\text{H}'$  ions formed pass into solution. The remaining  $\text{S}''$  ions increase the negative charge of the electrode.

Moore, Richter and Van Arsdel<sup>99</sup> advanced the viewpoint that all forms of sulfur do not act as poisons, but only as a sulfide it inhibits catalytic hydrogenation while sodium sulfate has no apparent effect. Vavon and Husson's<sup>139</sup> experimental evidence shows that for every substance there is a limiting weight of hydrogen sulfide above which hydrogenation ceases. This limit varies with the nature of the substance, other conditions being equal. It is independent of the weight of the substance and of the volume of the solvent, but it varies with the nature of the solvent, and with the quality of the platinum catalyst used. When the latter is constant, it is

proportional to the weight of the platinum used. Under certain conditions, the following limiting weights were obtained:

- 1.1 mg. for cyclohexene
- 0.8 mg. for nitrobenzene
- 0.5 mg. for cinnamic acid
- 0.4 mg. for acetophenone

Thus the platinum catalyst, after it had adsorbed 0.4 mg. of hydrogen sulfide would not hydrogenate acetophenone, but would catalyze the hydrogenation of cyclohexene.

Taylor and Capps<sup>131</sup> investigated the influence of various gaseous poisons on the activity of platinum catalysts used in the oxidation of ammonia to nitric oxide, and found that hydrogen sulfide had no appreciable effect. Decarri re,<sup>41</sup> on the other hand, claimed that hydrogen sulfide poisoned the catalyst.

Kubota and Joshikawa,<sup>77</sup> studying the poisoning effect of thiophene on nickel and copper catalysts, indicated that about one per cent of thiophene poisons nickel at 300  when used in hydrogenation of benzene. The rapidity with which nickel is poisoned was found to depend on the temperature at which it is reduced, the higher the temperature the more rapid the poisoning effect. Copper was not affected by thiophene.

Watanabe<sup>141</sup> investigated the poisoning effect of sulfur compounds on an iron catalyst in the decomposition of carbon monoxide and found that their poisoning effect was permanent and irremediable. Lee and Emmett<sup>84</sup> stated that hydrogen sulfide effected a definite increase in the conversion of ammonia to nitric oxide as compared with that obtained for ammonia-air mixtures. The reason for this increase in the conversion of ammonia by the addition of hydrogen sulfide has not been established. Andrews,<sup>8</sup> studying the action of oil impurities as catalytic poisons, investigated the behavior of sulfur-containing organic compounds, such as allyl-isothiocyanate, anticipating the inhibitory action of sulfur, implied also by a statement of Thomas,<sup>137</sup> that a small amount of hydrogen sulfide is able to prevent catalytic hydrogenation.

Maxted and Evans,<sup>92a</sup> comparing the catalytic poisoning of *w,w'*-propylenedithiol with that of *n*-propylthiol and *n*-butylthiol, find (1) that in spite of the increase in sulfur content the poisoning effect is decreased if even one sulfur atom is introduced at the second end of a hydrocarbon chain of a definite length; (2) if both sulfur atoms, on the contrary, are placed in neighboring positions, as in diethyl disulfide, then only a small change in poisoning effect takes place with respect to the corresponding compound with only one sulfur atom (diethyl sulfide). Therefrom it is concluded that, in agreement with the previously developed concept concerning the occurrence of the poison action, the decrease in poisoning in the first case is based on a limitation in the mobility of poison molecules anchored at two places of the catalyst surface. (3) The influences of a double bond or branching in the hydrocarbon chain upon the poisoning is small. (4) The poisoning effect of ring-structure sulfur compounds (thiophene, thiophenol, phenylethylthiol) and a thiourea derivative are compared one with another.

Maxted and Moon<sup>88b</sup> investigated the relationship between the degree of poisoning and the catalytic activity, adsorbed amount and adsorption velocity, in the case of a Pt catalyst used in the hydrogenation of crotonic acid. The poison was  $\text{H}_2\text{S}$ . By plotting the relative catalytic activity, which corresponds to the relative adsorbed amount (with respect to the catalytic activity, *i.e.*, adsorbed amount in the case of non-poisoned Pt) against the degree of poisoning (cc.  $\text{H}_2\text{S}$  per g. Pt), it is found that there is a far-reaching correspondence between the retrogression and adsorption decrease with increasing poisoning. The shorter the time interval after which the adsorbed amount is measured (1.5 and 10 min.) the better is the agreement. The rapid primary processes of adsorption are held responsible for the catalytic processes. The study of the kinetics of these primary processes confirms this assumption. The relative adsorption velocity (velocity constant from the adsorption velocity equation with respect to the velocity constant in case of non-poisoned Pt) plotted against the degree of poisoning (cc.  $\text{H}_2\text{S}$  per g. Pt) gives a straight line having almost the same slope as that showing the decrease of the relative catalytic activity of the same preparation with increasing poisoning. Concerning experiments at a lower pressure (0.0531–0.0671 mm. Hg) indications are found that the adsorption velocity in this case scarcely depends on the degree of poisoning, but is almost proportional to the instantaneous pressure.

### 3. Oxygen, Phosphorus and Arsenic

Kuhn,<sup>79</sup> discussing experiments in which the surface of the catalyst is poisoned by oxygen or air, assumed that the poisoning effect consists in the destruction of the active atomic hydrogen on which hydrogenation depends. Larson and Tour<sup>88</sup> and Almquist and Dodge<sup>7</sup> noted that oxygen compounds are poisons for iron catalysts in ammonia synthesis. The inhibiting effect of small concentrations of several different oxygen compounds was found to be proportional to their oxygen content in those cases in which the oxygen is converted into water under the conditions of the reaction. Almquist and Black,<sup>6</sup> in their interpretation of the poisoning action of oxygen on iron catalysts in ammonia synthesis, considered the poisoning action as being accompanied by the formation of iron oxide, the quantity of which increases with the use of the active promoted catalysts. (As promoters, they used 0.20%  $\text{K}_2\text{O}$ , 1.31%  $\text{Al}_2\text{O}_3$ , and a mixture of 0.25%  $\text{K}_2\text{O}$  and 1.05%  $\text{Al}_2\text{O}_3$ ). For all of the catalysts over the range of oxygen concentrations studied, a lowering of the ammonia concentration to a constant value resulted. The effects of equivalent concentrations of oxygen and water vapor were found to be identical with respect to the decrease in ammonia concentration and the formation of iron oxide. Maxted<sup>91</sup> emphasized the fact that the inhibitory action of poisonous elements depends not only on the form in which the poisonous element is present, but also on the reaction catalyzed, as well as on the catalyst present.

Arsenic compounds are strong poisons for the catalysts used in the contact process for the manufacture of sulfur trioxide. Arsenious oxide, due to its reduction to arsine, is a strong poison for catalytic hydrogenation with platinum as catalyst. This same poison has relatively little effect in

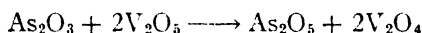
changing the activity of platinum when used in the decomposition of hydrogen peroxide. In this connection, it is known that some elements may act as poisons for certain catalytic reactions and as promoters for others. For example, bismuth, a strong poison for iron catalyst in catalytic hydrogenation, is one of the most active promoters for iron used in the oxidation of ammonia to nitric oxide.

A comparison of the behavior of vanadium catalysts used in oxidizing  $\text{SO}_2$  in sulfuric acid process, with respect to the influence of the poison  $\text{As}_2\text{O}_3$  upon the yield, was studied by Olsen and Maisner.<sup>103a</sup>

Table 9.  
(Olsen and Maisner)

Catalyst (%)	Reaction Charge (% of normal)	Temp. (°C.)	Initial Yield (%)	$\text{As}_2\text{O}_3$ Poison (%)	Decrease in Yield After Poisoning (%)
6.6% $\text{V}_2\text{O}_5$ on kieselguhr prepared from $\text{NH}_4\text{VO}_3 + \text{KOH}$ with usual activators.	167, which is 135 liters of gas mixture with 7% $\text{SO}_2$ per hour per 200 cc. catalyst.	480	99.16	12.61	95.05
			99.18	20.06	97.24
8.6% $\text{V}_2\text{O}_5$ activated with Ba. water glass as carrier.	132	480	99.16	6.0	90.17
5.7% $\text{V}_2\text{O}_5$ on kieselguhr.	140		98.16	6.9	89.00
$\text{V}_2\text{O}_5$ .	194	487	88.9	5.7	
	132	530	95.5		
	111	490	98.47		89.00

Siegert<sup>127a</sup> states that, in the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  over  $\text{V}_2\text{O}_5$  at  $450^\circ$ ,  $\text{As}_2\text{O}_3$  reacts with  $\text{V}_2\text{O}_5$  according to the equation:



and that at a higher temperature, such as  $500^\circ$ , and higher alkali content in the catalyst, namely, 12 instead of 6 per cent  $\text{K}_2\text{O}$ , the decrease in yield is smaller.

Calcium phosphate<sup>99</sup> is a promoter for nickel in the catalytic hydrogenation of sodium sulfate, while phosphorus as phosphine serves as an inhibitor. Taylor and Capps<sup>131</sup> found that phosphine present in a concentration as low as 3 parts per 100 million had a definitely injurious effect. Decarrière and co-workers<sup>41</sup> claimed that the poisoning effect of phosphine on platinum catalysts used for the oxidation of ammonia was so great that only 2 parts phosphine per 100 million parts of the gas mixture were sufficient to cause a distinct lowering of the conversion. However, the effect was of a temporary nature for, on removal of the poison, the conversion became normal. With 22 parts per 100 million parts, phosphine produced a permanently injurious effect.

Lee and Emmett's<sup>84</sup> results are in agreement with those of Decarrière and Taylor regarding the effect of phosphine on platinum catalysts in the oxidation of ammonia, the conversion changing from 90 to 95 per cent to 70 to 75 per cent in the presence of 0.00002 per cent of phosphine. Andrews,<sup>8</sup> choosing a phosphorus-containing organic compound, such as lecithin ( $\text{C}_{48}\text{H}_{84}\text{O}_9\text{NP}$ ), soluble in oil and considered an impurity of the oils which acts as a poison, obtained results indicating that if phosphorus in lecithin is a poison, then it plays a minor role, although the velocity of the

reaction is considerably reduced, the catalyst still having an appreciable activity after 40 minutes exposure to the poison.

Maxted and Marsden<sup>98a</sup> investigated the catalytic poisoning of simple hydrides of P, As, Sb and W with respect to Pt in catalytic hydrogenation.

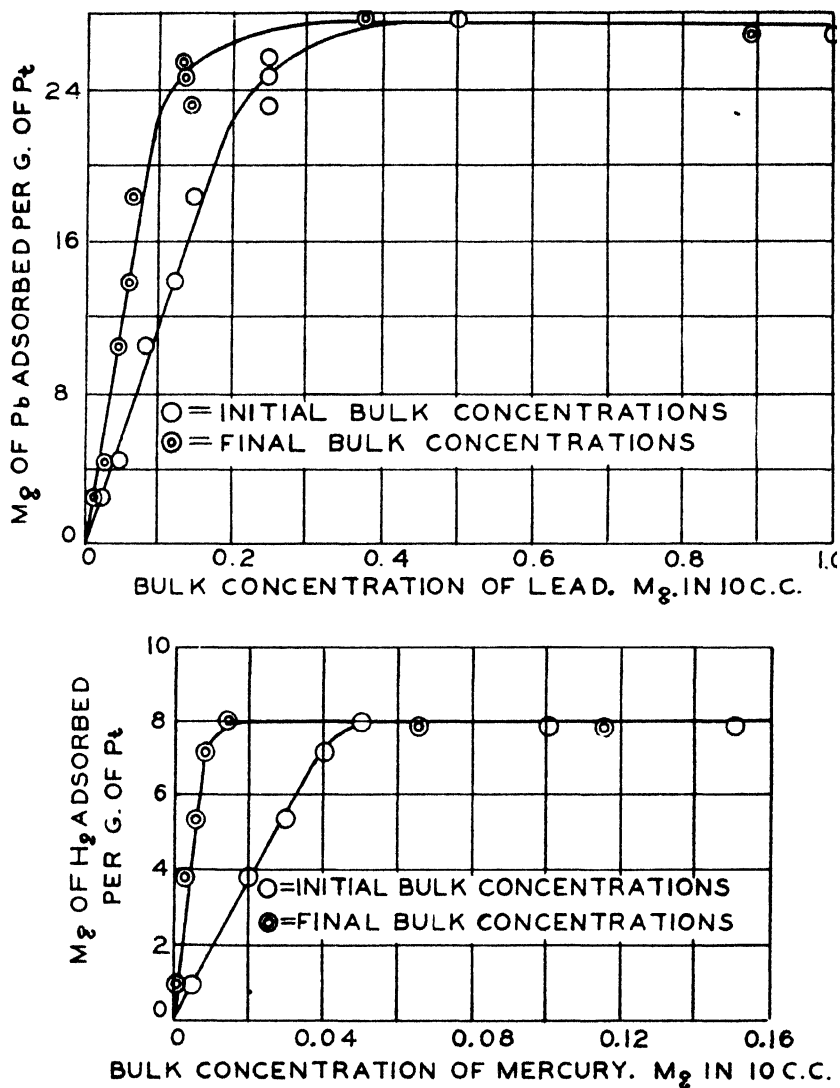


FIGURE 4.

They behave in the series P : As : Sb : W as 1.0 : 1.0 : 1.05 : 1.29 with regard to equal gram atom number of elements. The hydrides appear as such, or in the form of other compounds, and in the presence of catalytically activated H<sub>2</sub> they are converted into the corresponding hydrides. The



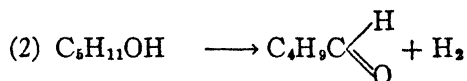
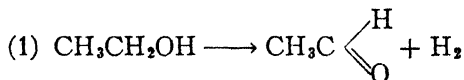
slightly greater poisoning effect of Sb and Bi were connected with the greater atomic radii of these elements, which in contrast to P and As exceed slightly the atomic radius of Pt.

#### 4. Other Poisons

Among the metals adsorbed by a catalyst which act as catalytic poisons, Maxted<sup>89</sup> placed special emphasis on the inhibitory influence of salts of lead and mercury in the catalytic decomposition of hydrogen peroxide and the hydrogenation of unsaturated compounds. He studied the adsorption of lead and mercury by finely dispersed platinum, the weight of lead and mercury adsorbed being plotted against its initial concentration, as shown in Figure 4.

Maxted stated that the inhibitory effect of a poison is measured by the decrease in the activity of the catalyst, and that this varies in the presence of a poison such as mercury or lead. For the first stage and the greater portion of the poisoning curve it is a linear function of the initial bulk concentration of the poison on the surface of the catalyst. According to Maxted, the free valence forces on the surface lattice of platinum saturated by a poison such as lead which evaporates with difficulty are not available for adsorption or association. The atoms of the poison adsorbed render a given number of the valence bonds inactive for normal catalysis.

Pease<sup>111</sup> showed that the adsorption of hydrogen by copper and the catalytic activity are markedly decreased by poisoning with a small amount of mercury. Ghosh and Bakshi,<sup>26</sup> referring to the poisoning action of mercuric iodide, stated that in very small amounts it diminishes considerably the velocity of the dehydrogenation of methyl alcohol, but the velocity of the decomposition of formaldehyde is very little affected. These investigators assumed that the two reactions, each involving different chemical and adsorption properties, occur at different points on the catalyst surface. The behavior of mercury as a poison in the dehydrogenation of methyl alcohol by copper catalyst differs from that of carbon disulfide and chloroform in that a very much smaller quantity of mercury is required for complete poisoning. Constable<sup>40</sup> pointed out that a poisoning effect may be produced also by ethyl and isoamyl alcohol obtained from fusel oil in reactions catalyzed with copper gauze, possibly through the formation of aldehydes:



Andrews,<sup>8</sup> in his article on oil impurities as catalytic poisons, discussed the probability that the solidification of some oils by hydrogenation with nickel occurs more rapidly than with others because of the action of fatty acids or some unsaponified material acting as poisons. The unsaponified material investigated in a very low grade of crude cod-liver oil added in an

amount of 2 per cent caused a marked decrease in the activity of the catalyst.

Alexejewski and Stosskind<sup>5a</sup> studied the influence of electrolyte additions upon the catalytic activity of  $\text{MnO}_2$  catalyst prepared in a suitable manner, and found that in all cases a poisoning of the catalyst took place, which was complete at 0.05 equivalent of the electrolyte to 1 mol  $\text{MnO}_2$ . The strength of poisoning increases in the sequence given; alkali ions:  $\text{Li}$ ,  $\text{K}$ ,  $\text{Na}$ ; alkaline earths:  $\text{Sr}$ ",  $\text{Ba}$ ",  $\text{Ca}$ "; anions:  $\text{NO}_3$ ',  $\text{Cl}$ ',  $\text{SO}_4$ ",  $\text{CO}_3$ ". The hydration of ions also increases in this sequence and therefore the degree of poisoning in the absence of water vapor is made dependent on the degree of hydration of adsorbed ions. According to these findings it is proposed that  $\text{MnO}_2$  catalysts be prepared according to methods in which only slightly hydrated or non-hydrated ions are adsorbed.

Raeder and Nilsen<sup>117a</sup> investigated the influence of various poisons for catalysts upon the hydrogen overvoltage, in order to determine quantitatively how far this influence upon overvoltage agrees with the generally assumed significance of active surface districts in heterogeneous cat-

Table 10. Poisons in Catalytic Syntheses.

Reaction	Poisons	Observer
Synthesis of $\text{NH}_3$ .	S, Se, Te, P, As and B act as contact poisons.	Brit. P. 19,249 (1910).
Synthesis of $\text{NH}_3$ with Fe as catalyst.	0.01% S renders catalyst inert; S, principal poison of the catalyst.	Haber: <i>Z. Elektroch.</i> , <b>16</b> , 244 (1910).
Synthesis of $\text{NH}_3$ with Fe-alumina-K oxide as catalyst.	Poisoned by small concentrations (0.32%) of $\text{H}_2\text{O}$ vapor; amount of $\text{O}_2$ retained by catalyst proportional to: $\sqrt{P_{\text{H}_2\text{O}}}/\sqrt{P_{\text{H}_2}}$ . Temperature, $450^\circ$ .	Emmett and Brunaker: <i>J. Am. Chem. Soc.</i> , <b>52</b> , 2682 (1930).
Synthesis of $\text{NH}_3$ with Pt catalyst.	Two parts $\text{PH}_3$ to 100 million parts of a mixture of gases decrease the reaction by several per cent.	Lee and Emmett: <i>Ind. Eng. Chem.</i> , <b>23</b> , 1090-1092 (1931).
Synthesis of $\text{NH}_3$ with U nitride as catalyst.	Water vapor (permanently poisons by converting the catalyst into a stable oxide which has no catalytic activity).	Ussatschew: <i>Z. Elektroch.</i> , <b>40</b> , 647 (1934).
Synthesis of $\text{NH}_3$ with Ti magnetite as catalyst I. and with Fe as catalyst II.	0.01-0.1% by vol. of $\text{O}_2$ or 0.02-0.1% by vol. of $\text{CO}$ ; catalyst I. is less sensitive to poison than catalyst II.	Epstein and Upolownikow: <i>Zhur. Khim. Prom.</i> , <b>10</b> , (3), 37-39 (1934).
Synthesis of ammonia over 3 different Fe catalysts; T. 400-525°; pressure, 300-800 atm.; space velocity 15,000, 30,000 and 45,000, respectively.	Water vapor (0.01-0.05%); a poisoning action of water vapor observed in all cases; the effect becomes greater with decreasing activity of the catalyst and increases with rising pressure and increase of conc.; with increasing temperature, however, in general a maximum is reached; the poisoning is interpreted as a decrease in active places on the surface.	Karnsolkin and Liwshitz: <i>Ibid.</i> , <b>14</b> , 244-49 (1937).
Synthesis of $\text{H}_2\text{O}$ from $\text{O}_2$ and $\text{H}_2$ over colloidal Pd.	Amalgamation renders the catalyst passive; however, the catalyst acts catalytically upon $\text{H}_2\text{O}_2$ in the presence of Hg.	Hartmann: <i>Ber.</i> , <b>51</b> , 711 (1918).
Combining of $\text{O}_2$ and $\text{H}_2$ with finely divided Ni.	$\text{C}_2\text{H}_4$ ; under these conditions no reduction to $\text{C}_2\text{H}_6$ takes place.	Sandonnini: <i>Gazz. chim. ital.</i> , <b>52</b> , 1, 394 (1922).
Synthesis of $\text{H}_2\text{O}$ with Ni and Cu catalysts.	An undefined oxide; side reaction leads to poisoning of catalyst.	Smith: <i>J. Phys. Chem.</i> , <b>32</b> , 719-733 (1928).
Synthesis of $\text{H}_2\text{O}$ with colloidal Pd (which transfers $\text{H}_2$ ) as catalyst.	Amalgamation renders the catalyst passive.	Paal and Hartmann: <i>Ber.</i> , <b>51</b> , 711 (1918).

alysis.<sup>139a</sup> Using as electrode material platinized Pt and black nickelated Ni, and using as poisons Hg, As, Pb and Cu, they found that in the electrolytic evolution of H<sub>2</sub> the same significance had to be ascribed to active surface development as in the ordinary heterogeneous catalysis with solid catalysts.

It is assumed that for a given cathode H<sub>2</sub> liberation occurs on the most active, as well as the most approachable, surface parts, where the energy hump between the H ion and the neutral hydrogen molecule is lowest. By precipitation of foreign metals, the most active surface points will be occupied, and therefore the minimum heights of the energy hump will be raised. This in turn will result in an increase in the overvoltage. Thus the highest energy hump lies between the hydrated ion and the discharged atom, the discharge overvoltage determining the partial process taking place (Smits-Volmer).

Table 11. Poisons in Catalytic Decomposition.

Reaction	Poisons	Observer
Decomposition of H <sub>2</sub> O <sub>2</sub> by Pt catalyst.	Hg.	Bredig and Müller von Berncek: <i>Z. phys. Chem.</i> , <b>31</b> , 327 (1899).
Decomposition of H <sub>2</sub> O <sub>2</sub> by colloidal Pt catalyst.	3x10 <sup>-4</sup> gr. molecules of H <sub>2</sub> S or more per liter poison the reaction almost completely.	Bredig and Müller von Berncek: <i>Ibid.</i> , <b>31</b> , 327 (1899). Bredig and Ikeda: <i>Ibid.</i> , <b>37</b> , 8 (1901).
Decomposition of H <sub>2</sub> O <sub>2</sub> by colloidal Pt catalyst.	0.001 mol HCN per liter destroys catalytic activity almost wholly; iodine also poisons this reaction, but the activity of the partially poisoned Pt catalyst, instead of increasing during the reaction as with HCN, gradually decreases due to the removal of a certain amount of the catalyst by chemical combination with the poison.	Bredig and Müller von Berncek: <i>Ibid.</i> , <b>31</b> , 327 (1899). Bredig and Ikeda: <i>Ibid.</i> , <b>37</b> , 8 (1901).
Decomposition of H <sub>2</sub> O <sub>2</sub> by Pt catalyst.	I <sub>2</sub> and HgCl <sub>2</sub> , strong poisons.	Jabczynski: <i>Ibid.</i> , <b>64</b> , 748 (1908).
Decomposition of H <sub>2</sub> O <sub>2</sub> by colloidal Pt catalyst.	Narcotics form an isolated layer around the Pt particles; they decrease the degree of dispersion.	Meyerhof: <i>Pflüger's Arch.</i> , <b>157</b> , 307 (1914). Warburg: <i>Ergebn. Physiol.</i> , <b>14</b> , 298 (1914).
Decomposition of H <sub>2</sub> O <sub>2</sub> by Pt black catalyst.	Hg ions.	Maxted and Lewis: <i>J. Chem. Soc.</i> , <b>1933</b> , 502.
Decomposition of H <sub>2</sub> O <sub>2</sub> by Pt.	P <sub>2</sub> O <sub>5</sub> (volatile admixture of P <sub>2</sub> O <sub>5</sub> used for drying in case of a very strong evacuation).	Roiter and Schafran: <i>Zhur. Fiz. Khim.</i> , <b>4</b> , 461-464 (1933).
Decomposition of H <sub>2</sub> S by Pt black catalyst with evolution of H <sub>2</sub> .	H <sub>2</sub> not adsorbed by sulfurized Pt.	Maxted: <i>J. Chem. Soc.</i> , <b>115</b> , 1050 (1919).
Decomposition of CO by Fe catalyst.	Naphthalene condensed on the surface of the catalyst.	Watanabe: <i>Bull. Inst. Phys. Chem. Res. (Tokyo)</i> , <b>1</b> , 102-103 (1928).
Decomposition of nitramide with Pt and Au sols as catalysts.	Strong acids, iodine, dextrin, glucose.	King: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 144-154 (1938).
Decomposition of HCHO.	CHCl <sub>3</sub> and CS <sub>2</sub> .	Ghosh and Bakshi: <i>J. Ind. Chem. Soc.</i> , <b>3</b> , 415 (1926).
Decomposition of formic acid: 1. HCOOH → CO + H <sub>2</sub> 2. HCOOH → CO + H <sub>2</sub> O over Ni catalyst.	H <sub>2</sub> S, SO <sub>2</sub> , H <sub>2</sub> SO <sub>4</sub> , P <sub>2</sub> O <sub>5</sub> , As <sub>2</sub> O <sub>3</sub> , As <sub>2</sub> O <sub>5</sub> .	Platonow and Tomilow: <i>Zhur. Obshchei Khim.</i> , <b>8</b> , (70), 346-356 (1938).

Table 12. Poisons in Catalytic Oxidation.

Reaction	Poisons	Observer
Oxidation of $\text{NH}_3$ with Pt catalyst.	$\text{PH}_3$ and $\text{H}_2\text{S}$ ; 10 parts $\text{PH}_3$ in 1 million Pt black gauze.	Taylor and Capps: <i>J. Ind. Eng. Chem.</i> , 11, 27 (1919).
Oxidation of $\text{NH}_3$ with Pt catalyst.	1 part $\text{PH}_3$ in 5 million; 70% yield obtained with a pure gas; 1 part $\text{PH}_3$ in 5 thousand; about 4% of the normal yield is obtained; in the presence of a small amount of $\text{H}_2\text{S}$ , the toxic effect of $\text{PH}_3$ is neutralized.	Decarrière: <i>Compt. rend.</i> , 174, 460 (1922); 174, 756 (1922).
Oxidation of $\text{NH}_3$ with Fe.	$\text{O}_2$ produces a poisoning effect.	Almquist and Black: <i>J. Am. Chem. Soc.</i> , 48, 2814-2826 (1926).
Oxidation of $\text{NH}_3$ .	Water vapor (0.08%-0.64%) under high pressure (up to 100 atmospheres) and temperature of $450^\circ$ produces a poisoning effect; the amount of $\text{O}_2$ retained by the catalyst is proportional to $\text{PH}_3/\text{O}_2$ ; a very active catalyst may retain more $\text{O}_2$ .	Emmett and Brunaker: <i>Ibid.</i> , 52, 2682-2693 (1930).
Conversion of $\text{NH}_3$ into $\text{HNO}_3$ .	$\text{PH}_3$ ; 1 part in 10 million reduced the yield from 94% to 58%; 1 part in 50 million yielded 77%.	Brush (quoted by Perley): <i>J. Ind. Eng. Chem.</i> , 12, 5 (1920).
Conversion of $\text{NH}_3$ into $\text{HNO}_3$ by Fe catalyst.	Bi.	Maxted: <i>Chem. Age</i> , 7, 816-818 (1922).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ with Pt catalyst.	A fraction of a per cent As, Pb, or Hg.	Maxted: <i>J. Chem. Soc.</i> , 121, 1760 (1922); 127, 73 (1925); 133, 1600 (1928); 145, 672 (1934).
Oxidation of $\text{SO}_2$ over V catalyst.	$\text{As}_2\text{O}_3$ oxidized to $\text{As}_2\text{O}_5$ which, when adsorbed in a definite amount, decreases the activity rapidly; poisoning effect irreversible.	Adadurov and Kusminskaia: <i>Zhur. prikl. Khim.</i> , 5, 722-735 (1932).
Oxidation of $\text{SO}_2$ over $\text{Cr}_2\text{O}_3$ — $\text{SnO}_2$ — $\text{BaO}$ or $\text{V}_2\text{O}_5$ — $\text{SnO}_2$ — $\text{BaO}$ catalysts; the conversion follows according to the scheme: $3\text{SO}_2 = \text{SO}_3 + \text{S}$ $\text{S} + \text{O}_2 = \text{SO}^* + \text{O}^*$ $\text{SO}^* + \text{O}_2 = \text{SO}_3$ $\text{SO}_2 + \text{O}^* = \text{SO}_3$ , etc.	$\text{As}_2\text{O}_3$ . The decrease in activity is due to clogging of the active surface of the catalyst with $\text{As}_2\text{O}_5$ originating by oxidation of $\text{As}_2\text{O}_3$ . Using a mixture of CO (generator gas) with $\text{H}_2$ , the contact mass (whose activity has been decreased through reduction of $\text{SnO}_2$ ) may be regenerated. Water vapor as it appears in plant production does not (influence) decrease the activity, but by saturation of the $\text{SO}_2$ -air mixture with water vapor, a decrease in catalytic activity is observed. The activity may be re-established by eliminating the water vapor supply. Likewise while moistened HCl decreases the catalytic activity of Cr catalyst, the dry HCl gas causes no decrease in the activity.	Adadurov and Gernet: <i>Ibid.</i> , 8, 612-627 (1935).
Oxidation of $\text{SO}_2$ over V catalyst.	As.	Adadurov: <i>Trans. Mendeleev Cong. Theor. Appl. Chem.</i> , 6th Cong. 2, 154 (1935).
Oxidation of $\text{SO}_2$ by ozone over $\text{MnSO}_4$ .	Phenol. Manganic acid is formed. (In aqueous phenol solution it is oxidized by ozone to quinone, which has no poisoning action.)	Kashtanov and Ryshov: <i>Zhur. Obschei. Khim.</i> , 6 (68), 732-747 (1936).
Oxidation of iodides by persulfates; N, N-di-methyl- <i>p</i> -phenylenediamine and tetramethyl- <i>p</i> -phenylenediamine acts as a catalyst.	Cystine, malonic acid ester. These poisons differ in electrochemical properties from the poison previously investigated, namely, $\text{Na}_2\text{S}_2\text{O}_4$ , because they are weak electrolytes; however, they reduce elemental iodine with high velocity.	Afanasiew: <i>Zhur. Fis. Khim.</i> , 11, 242-247 (1938).
Oxidation of CO over Hopcalite (70% $\text{MnO}_2$ +30% $\text{CuO}$ ), in two stages. (1) increase in activity by oxidation of CO by the oxygen of $\text{MnO}_2$ causing irreversible decomposition of the latter; (2) the normal oxidation process of CO with molecular oxygen.	2.7% $\text{H}_2\text{O}$ ; an increase in adsorbed water on the Hopcalite surface causes a linear decrease in its activity, whereby complete poisoning occurs independently of the temperature of adsorption.	Schurmowskaja and Bruns: <i>Ibid.</i> , 9, 301-312 (1937).

Table 12 (Continued).

Reaction	Poisons	Observer
Oxidation of CO; 60% MnO <sub>2</sub> and 40% CuO most active catalysts; rapid action at 0°.	CO <sub>2</sub> adsorbed by dry ppt. oxide, but not as a poison; a much higher temperature required for either of the individual constituents.	Taylor and Benton: <i>J. Am. Chem. Soc.</i> , <b>45</b> , 887 (1923).

Table 13. Poisons in Catalytic Hydrogenation.

Reaction	Poisons	Observer
Catalytic action of Pt on a mixture of C <sub>2</sub> H <sub>4</sub> and H <sub>2</sub> .	Poisoning of Pt catalyst by CO almost complete.	Lunge and Harbeck: <i>Z. anorg. Chem.</i> , <b>16</b> , 50 (1896).
Displacement of adsorbed H <sub>2</sub> from Pt sols by Hg.	Poisoning of colloidal Pt by Hg.	Paal and Hartmann: <i>Ber.</i> , <b>51</b> , 1711 (1918). Paal and Steger: <i>Ber.</i> , <b>51</b> , 1743 (1918).
Catalytic hydrogenation of Na <sub>2</sub> SO <sub>4</sub> .	S as a sulfide; P as PH <sub>3</sub> .	Moore, Richter and Van Arsdel: <i>J. Ind. Eng. Chem.</i> , <b>9</b> , 451 (1917).
Catalytic hydrogenation.	Bi.	Maxted: <i>Chem. Age</i> , <b>7</b> , 816 (1922).
Catalytic hydrogenation of H <sub>2</sub> O <sub>2</sub> with Pt catalyst.	As <sub>2</sub> O <sub>3</sub> .	Maxted: <i>Chem. Age</i> , <b>7</b> , 816 (1922).
Hydrogenation over Ni catalyst.	Traces of Cl, Br, I, or S compounds present in the metal.	Sabatier: <i>Ber.</i> , <b>44</b> , 1984 (1911).
Hydrogenation, using Ni catalyst.	Oxy-tearic, maleic, tartaric and citric acids, Ca(OH) <sub>2</sub> , boric acid, potash, ammonium molybdate, red phosphorus, lecithine, morphine, strychnine, amygdaline, cyanides.	Seiichiden: <i>J. Soc. Chem. Ind. Japan</i> , <b>21</b> , 898 (1918).
Hydrogenation with Ni catalyst.	CO present in hydrogen.	Maxted: <i>Chem. News</i> , <b>117</b> , 73 (1918).
Catalytic hydrogenation with Ni catalyst.	CO has affinity for Ni only below 180° C.; above this temperature, the latter is reduced to CH <sub>4</sub> .	Taylor and Burns: <i>J. Am. Chem. Soc.</i> , <b>43</b> , 1273 (1921). Taylor and Gauger: <i>Ibid.</i> , <b>45</b> , 920 (1923). Taylor and Benton: <i>Ibid.</i> , <b>45</b> , 887 (1923).
Hydrogenation of CO to increased proportion of higher alcohols.	Alkali, as well as Rb, poison the Mn chromite catalyst.	Morgan, Hardy and Procter: <i>J. Soc. Chem. Ind.</i> , <b>51</b> , 1T (1932).
Hydrogenation of ethylene over MoS <sub>2</sub> -ZnO catalyst (ratio 95 : 5) (in lengthy experiments the catalyst keeps its activity at temperatures up to 320°; further increase in temperature up to 400° leads to partial deactivation of the catalyst due to an activated adsorption of C <sub>2</sub> H <sub>4</sub> , which leads to a condensation with formation of high molecular weight polymerization products at the catalyst surface. Also there is a possibility of decomposition of C <sub>2</sub> H <sub>4</sub> at this temperature, with formation of soot).	O <sub>2</sub> ; a thermal treatment of the catalyst in H <sub>2</sub> increases its activity by 20-25%.	Masslajski and Nemzow: <i>Doklady Akad. Nauk U.S.S.R.</i> , <b>11</b> , 404-409 (1935).
Hydrogenation of ethylene over Ni, Cr <sub>2</sub> O <sub>3</sub> and MoS <sub>2</sub> catalysts; poisoning the Ni catalyst at 250° drops the conversion to 52%. However, the poisoning is temporary. Cr <sub>2</sub> O <sub>3</sub> catalyst, prepared by precipitating Cr(NO <sub>3</sub> ) <sub>3</sub> with NH <sub>3</sub> , is activated by the poison. The conversion increases from 22.6% to 35.0%. MoS <sub>2</sub> catalyst prepared by reduction of MoS <sub>3</sub> at 50 atm., 375°, and for 4 hrs. with H <sub>2</sub> in an autoclave at 425° shows a decrease in reduction activity of about 10-20% with increased polymerization (C on the contact about 3%); T. 425° considerable poisoning; yield, 11%.	CO (1.0%), HCl, NH <sub>3</sub> , or pyridine. CO (contact poison). HCl (0.8%). HCl (0.93%). HCl (0.8%).  NH <sub>3</sub> (0.98%), pyridine (0.75%).	Anissimow and Polozow: <i>Zhur. Priklad. Khim.</i> , <b>11</b> , 297-300 (1938).
Hydrogenation of crotonic, oleic and benzoic acids with a Pt catalyst.	Hg ions and CS <sub>2</sub> .	Maxted and Stone: <i>J. Chem. Soc.</i> , <b>1934</b> , 26-29; <b>1934</b> , 672-674.

Table 13 (Continued).

Reaction	Poisons	Observer
Catalytic hydrogenation of alcohols with Cu catalyst.	Cu catalyst may poison itself at a moderate temperature.	Constable: <i>J. Chem. Soc. (London)</i> , 131, 2995-3000 (1927).
Hydrogenation of $C_6H_6$ to cyclohexane.	Thiophene.	Roberti: <i>Gazz. chim.</i> , 63, 46 (1933).
Hydrogenation of nitrobenzene.	$NiSO_4$ ; 2 parts $NiSO_4$ in 100 parts $Ni(NO_3)_2$ limits reduction to aniline and prevents formation of cyclohexyl compounds.	Kiyoshi and Joshikawa: <i>Sci. Papers Inst. Phys. Chem. Res. (Tokyo)</i> , 25, 235-301 (1934).
Hydrogenation of benzene with Ni as compared with Cu-Ni; addition of Cu to Ni considered as effecting a decrease in very active places and an increase in less active places.	Thiophene.	Kiyoshi and Joshikawa: <i>Bull. Inst. Phys. Chem. Res. (Tokyo)</i> , 14, April 22, 1935.
Hydrogenation of phenol to cyclohexanol.	Bromine.	Sabatier and Maible: <i>Compt. rend.</i> , 153, 160 (1911).
Hydrogenation of pinene over Pt black.	Alcohol, ether, ethyl acetate, or formic acid (serving as solvents for pinene).	Boeseken and van der Weide: <i>Rec. trav. chim.</i> , 35, 260 (1916).
Catalytic hydrogenation of oils with Ni catalyst.	$SO_2$ , most active poison; in all probability due to its catalytic reduction to $H_2S$ , according to Maxted.	Thomas: <i>J. Soc. Chem. Ind.</i> , 39, 15T (1920).
Reduction of geraniol to citronellol to tetrahydrogeraniol with Pt-PtO <sub>2</sub> .	$FeSO_4$ or Zn acetate in large amounts.	Adams and Garvey: <i>Ibid.</i> , 48, 477 (1926).
Reduction of CO to $CH_4$ under ordinary pressure over Ni on pumice (Mo, Mo oxides, Mo sulfides on silica gel stable toward S compounds).	$H_2S$ ; poisoned after 3 hrs. activity to about 1/5 of initial value.	Sebastian: <i>Congr. Chim. in Brussels</i> , 15, II, 875-885 (1935).
Reduction of nitrobenzene over Ni catalyst from Ni-Al alloy.	$NiCl_2$ .	Reasenber, Lieber and Smith: <i>J. Am. Chem. Soc.</i> , 61, 384-387 (1939).
Dehydrogenation of $CH_3OH$ .	Mercuric iodide.	Ghosh and Bakshi: <i>J. Indian Chem. Soc.</i> , 3, 415 (1926).
Dehydrogenation of $CH_3OH$ .	$CS_2$ , $CHCl_3$ and Br; for complete poisoning, an equal number of atoms of Pt, S, Cl and Br are necessary.	Bakshi: <i>Ibid.</i> , 6, 749 (1929).

Table 14. Poisons in Various Catalytic Reactions.

Reaction	Poisons	Observer
Gaseous catalysis.	CO has a greater poisoning effect on the catalyst than $CO_2$ .	Pickles: <i>Chem. Age</i> , 7, 164-165 (1922); 6, 586 (1922).
Hydrogenation of oils with Ni catalyst.	Oil impurities as catalyst poisons.	Andrews: <i>Chem. Trade J.</i> , 84, 277-278, 302-303, 351-352, March 22, 1929.
Alcoholic fermentation of sugar; catalysts, Fe, Co, Ni and Mn.	Ni has a greater poisoning effect than Fe, Co and Mn; 5.5 times less sugar is fermented in the presence of $Fe^{++}$ than in the presence of $Fe^{+++}$ .	Rosenblat and March: <i>Ukrainsk. Chem. Zh.</i> , 5, (Tech. Part.), 127-138 (1930).
Platinized Pt and black nickelized Ni used as electrodes in electrolysis.	Hg, As, Pb and Cu poisons for electrolytic development of $H_2$ ; for a given cathode, the $H_2$ development occurs predominantly on most active and approachable surface parts where the energy hump between hydrated H ions and the neutral $H_2$ molecules is the lowest.	Raeder and Nilsen: <i>Norges tekn. Høiskole Avhandl. til 25 Ars Jubileet</i> , 263-279 (1935).
Poisoning of Pt in hydrogen electrodes in KCl and HCl solutions.	$H_2S$ .	Yablizynska-Jedrzejewska: <i>Roczniki Chem.</i> , 16, 307-312 (1936).
Poisoning of the $H_2$ and $O_2$ electrodes in $H_2SO_4$ and KOH solutions.	KCN, $As_2O_3$ , $H_2S$ , quinine and benzene (compounds believed to be formed between Pt and poisons).	Isgarischew and Koldaewa: <i>Z. Elektr.</i> , 30, 83 (1924).

Table 14 (Continued).

Reaction	Poisons	Observer
Reduction of unsaturated organic compounds with colloidal Pt and Pd.	If the layer surrounding the catalyst can not be penetrated by the reacting components (diffusion of $H_2$ ), poisoning takes place.	Boeseken and Weide: <i>Rec. trav. Chim. Pays-Bas</i> , <b>35</b> , 260 (1916).
Catalytic action of Pt black.	Poisoned by traces of grease.	Faraday: <i>Exp. Res. on Electricity</i> , <b>1</b> , 185 (1939).
Adsorption of hydrogen by platinized asbestos.	Poisoned by traces of grease (vapors).	Pollard: <i>J. Phys. Chem.</i> , <b>27</b> , 356 (1923).
Catalytic action of Pt on mixtures of air with $H_2$ or ether.	Hydrides of S, Te, Se, P, As and Sb.	Schönbein: <i>J. prakt. Chem.</i> , <b>29</b> , 238 (1843).
Catalytic action of Pt.	Poisoning effect of Pb apparently proportional to its amount, i.e., 1 mg. Pb poisons 8.8 mg. Pt.	Maxted: <i>J. Chem. Soc.</i> , <b>117</b> , 1280, 1501 (1920); <b>119</b> , 225 (1921).
Catalytic action of Pt.	Pt surface poisoned even at very low CO pressure (few cm.), rendering $H_2$ and other gases ineffective.	Taylor and Burns: <i>J. Am. Chem. Soc.</i> , <b>42</b> , 1285 (1921).
Catalytic action of Pt black.	$CS_2$ .	Vavon and Husson: <i>Compt. rend.</i> , <b>175</b> , 277-279 (1922).
Catalytic action of Pt black.	Chlorine.	Boswell and Bayley: <i>J. Phys. Chem.</i> , <b>29</b> , 11-19 (1925).
Catalytic action of Pt.	Pb and Hg.	Maxted: <i>J. Chem. Soc.</i> , <b>127</b> , 73-74 (1925).
Catalytic action of Pt.	$As_2O_3$ .	Maxted and Dunsby: <i>Metal-borser</i> , <b>18</b> , 1742-1743 (1927).
Adsorption of $H_2$ by Pd.	Traces of fatty vapors from the air or grease from the stopcocks.	Berliner Wied. Ann., <b>35</b> , 903 (1888).
Catalytic action of Pd hydrosol.	Hg displaces $H_2$ .	Paal and Steger: <i>Ber.</i> , <b>51</b> , 1743 (1918).
Catalytic hydrogenation with Pd.	Co, Hg and $H_2S$ poisons for the occlusion of $H_2$ .	Maxted: <i>Chem. Age</i> , <b>7</b> , 816-818 (1922).
Gaseous catalysis with Cu catalyst.	Cu poisoned by CO effects a change in the adsorption of $C_2H_4$ and $H_2$ .	Griffin: <i>J. Am. Chem. Soc.</i> , <b>49</b> , 2136-2145 (1927).
Catalytic action of Cu and Ni.	Thiophene.	Kubota and Joshikawa: <i>J. Chem. Soc. Japan</i> , <b>2</b> , 45-63 (1925).
Catalytic action of Ni.	Thiophene.	Kubota and Joshikawa: <i>Sci. Papers Inst. Phys. Chem. Res.</i> , (Tokyo), <b>3</b> , 35-50 (1925).
Catalytic action of reduced Ni oxide.	$Cl_2$ does not poison the catalyst when Ni is prepared from $NiCl_2$ , which is highly volatile; complete reduction occurs at $250^\circ$ .	Boswell and Bayley: <i>J. Phys. Chem.</i> , <b>29</b> , 11-19 (1925).
Catalytic action of Ni.	Cobalt.	Kusma and Uno: <i>Bull. Inst. Phys. Chem. Res. (Tokyo)</i> , <b>2</b> , 50-51 (1929).
Dissociation of $H_2$ by a heated W filament.	$O_2$ (decreases the adsorption of $H_2$ ).	White and Benton: <i>J. Phys. Chem.</i> , <b>35</b> , 1784-1789 (1931).
Catalytic action of $Al_2O_3$ .	It is assumed that thiophene, which acts as a poison, changes the multiplet action described by models.	Langmuir: <i>J. Am. Chem. Soc.</i> , <b>38</b> , 2272 (1916).
		Kubota and Imanaka: <i>Bull. Chem. Soc. Japan</i> , <b>4</b> , 211-220 (1929).

## A COMPARISON OF THE PROPERTIES OF PROMOTERS AND POISONS

## Introduction

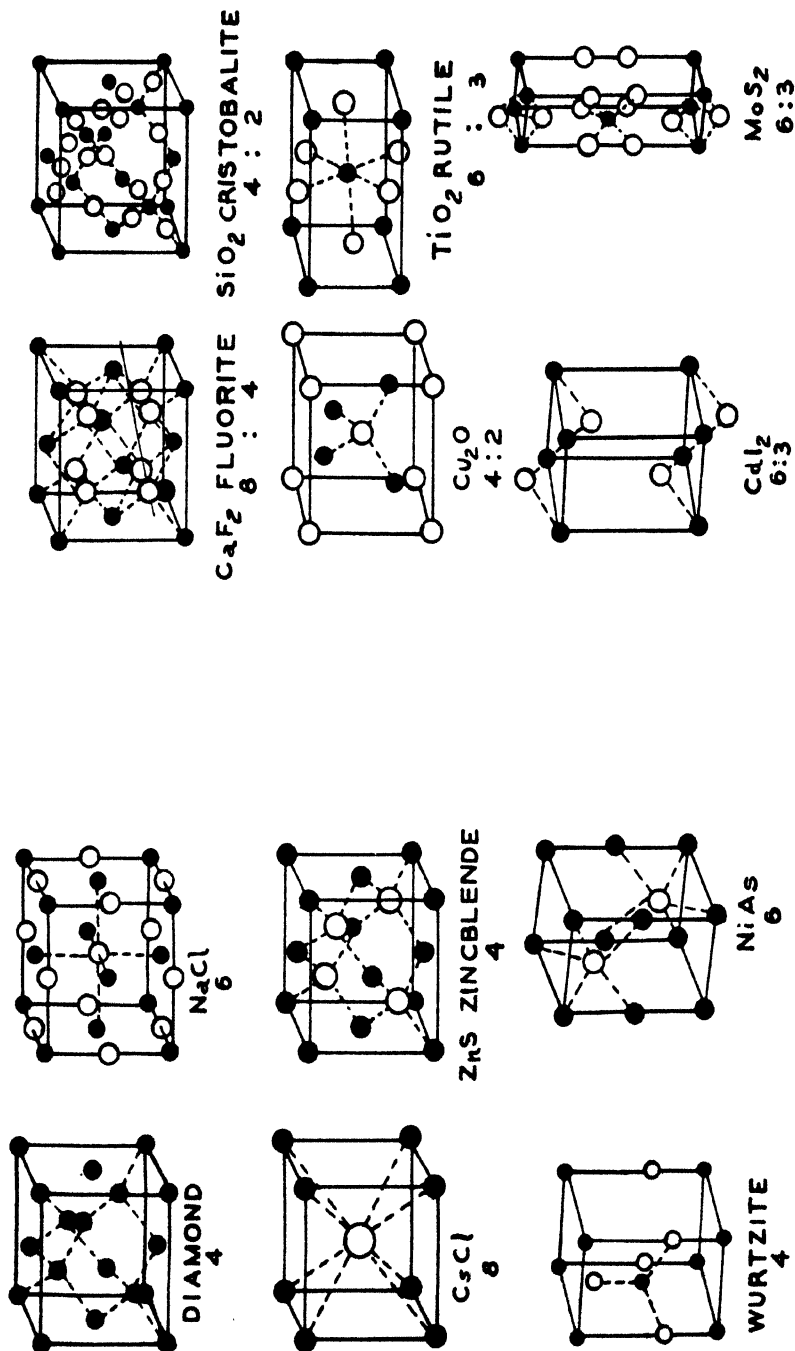
The systematic study of the literature on catalysis, particularly with reference to catalytic reactions activated by a promoter, or retarded or prevented by poisons, permits a correlation of the experimental evidence on the subject from which some general conclusions may be drawn. The sub-

(Text continued on page 408)

**Table 1.**  
*Promoters*

[illegible]





Diamond and AX Compounds

AX<sub>2</sub> Compounds

(Numbers indicate Co-ordination in each case)

Table 2. Common Structure Types.\*

\*From "Crystal Chemistry," by H. O. Hassel, London, W. Heinemann, Ltd., 1935.

Table 3.  
*Promoters for Nickel Catalysts*

Catalyst:	Ni cub.			Catalyst:	NiH <sub>2</sub>
Promoters:	6.55			Promoters:	C <sub>2</sub> H <sub>5</sub> OH CH <sub>3</sub> OH
		Catalyst: NiO cub. NaCl type 11.0			
		Promoters:			
		Elements			
Cu	Ag	Tl	Th		
7.05	10.13	16.9	19.7		
		Oxides			
BeO	CeO <sub>2</sub>	ThO <sub>2</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>
hex.	cub.	cub.	hex.	trig.	hex.
8.3	23.9	26.4	22.7	25.1	29.0
		Carbonates			
		Na <sub>2</sub> CO <sub>3</sub> monocl.			
		41.0			
		Sulfates			
		Na <sub>2</sub> SO <sub>4</sub> rhomb.			
		52.2			
		Nitrates			
		NaNO <sub>3</sub> trig.			
		36.7			
		Phosphates			
		Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> trig.			
		99.3			
		Catalyst: Co hex.			
		6.58			
		Promoters:			
		Elements			
Cu	Ag	ThO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>		
7.05	10.13	cub.	hex.		
		Oxides			
BeO	UO <sub>2</sub>	ThO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>		
hex.	cub.	cub.	trig.		
8.3	24.8	26.4	29.0		
		Phosphates			
		KPO <sub>3</sub> Na <sub>3</sub> PO <sub>4</sub>			
		hex.			
		52			

*Promoters for Cobalt Catalysts*  
Catalyst:

CoO	CoO		
cub.	cub.		
NaCl type	NaCl type		
11.65	11.65		
		Oxides	
BeO	UO <sub>2</sub>	ThO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>
hex.	cub.	cub.	trig.
8.3	24.8	26.4	29.0
		C type	
		Senarmonite type	
		50	
		39.2	

Table 4.  
*Promoters for Copper Catalysts*

Catalyst: Cu cub.  
7.05

Catalyst: CuO monocl.  
12.0

Catalyst: CuSO<sub>4</sub> tricl. (rhomb.)  
44.5

Promoters:

Promoters:

Elements				
Ni	Co	Cr	Mn	Ag
cub.	hex.	cub.	cub.	cub.
6.55	6.58	7.2	7.26	10.13
Th	Ce			
cub.	cub.			
19.7	20.2			

Oxides				
MgO	FeO	CuO	ZnO	MnO <sub>2</sub>
cub.	cub.	cub.	hex.	tetrag.
NaCl	NaCl	PtS	ZnS	TiO <sub>2</sub>
type	type	type	type	type
11.3	11.8	12.0	14.3	17.0

PbO <sub>2</sub>	
tetrag.	
Rutile type	
24.6	

Carbonates	
CuCO <sub>3</sub>	MgCO <sub>3</sub> ZnCO <sub>3</sub>
hex.	hex.
10.13	27.3
	27.6

Oxides				
MgO	FeO	CaO	BaO	HgO
cub.	cub.	cub.	cub.	rhomb.
	Sodium chloride			ZnS
	type			type
11.3	11.8	16.7	25.7	19.3

MnO <sub>2</sub>	
tetrag.	
TiO <sub>2</sub> type	
17.0	

Sulfates	
SrSO <sub>4</sub>	BaSO <sub>4</sub>
rhomb.	rhomb.
Baryta type	
45.9	51.1
	56.1

Chromates	
BaCrO <sub>4</sub>	
monocl.	
56.1	

*Promoters for Iron Catalysts*

Catalyst: Fe  
cub.  
7.05

Catalyst: FeO  
cub.  
11.8

Catalyst: Fe<sub>2</sub>O<sub>3</sub>  
hex.  
30.3

Catalyst: FeSO<sub>4</sub>  
monocl.  
45

Promoters:

Promoters:

Promoters:

## Elements

Ni	Co	Cu	Cr	Mn
cub.	hex.	cub.	cub.	cub.
6.55	6.58	7.05	7.2	7.26
W	Ag	Th	Ce	Bi
cub.	cub.	cub.	cub.	trig.
9.5	10.13	19.7	20.2	21.0

## Oxides

BeO	UO <sub>2</sub>	ThO <sub>2</sub>	Bi <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> O <sub>3</sub>
hex.	cub.	cub.	C type	cub.
8.3	24.8	26.4	50	51.4

## Oxides

BeO	MgO	UO <sub>2</sub>	ThO <sub>2</sub>
hex.	cub.	cub.	cub.
8.3	11.3	24.8	26.4
ZnS	NaCl	CaF <sub>2</sub>	CaF <sub>2</sub>
type	type	type	type
8.3	11.3	24.8	26.4

## Oxides

CuO	CeO <sub>2</sub>	ThO <sub>2</sub>
tricl.	cub.	cub.
PtS	CaF <sub>2</sub>	type
type	23.9	26.4
12.0		

Catalyst: Fe<sub>2</sub>O<sub>3</sub>

Promoters:

Cr<sub>2</sub>O<sub>3</sub> hex.  
29.0

Sb<sub>2</sub>O<sub>3</sub>  
hex.  
39.2

Senarmontite  
type  
39.2

## Oxides

BeO	MgO	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O
hex.	cub.	hex.	cub.
8.3	11.3	25.7	40

CaF<sub>2</sub> type

stances functioning as promoters or poisons may also be classified with respect to their physico-chemical characteristics. The relationship between the properties of the substance and its action either as a promoter or poison will permit a logical method to be developed for selecting promoters specific for the catalyst and the type of reaction desired, and also suggests measures for preventing the action of poisons.

### Explanation of Tables

Table 1 presents a list of promoters. The largest group of promoters is that of the oxides followed by a group of elements, chlorides, organic compounds, sulfates, hydroxides, carbonates, phosphates, and nitrates. The spatial factor and the crystallographic type are given; it will be noted that the cubic and hexagonal systems prevail. The sodium chloride, calcium fluoride, magnesium chloride, Wurtzite and Rutile types are among those frequently occurring among promoters (Table 2). (Text continued on page 412)

Table 5.

#### *Promoters for Platinum Catalysts*

Catalyst: Pt cub. 9.03			Catalyst: PtO			Catalyst: PtO—Pt black
Promoters:			Promoters:			Promoters:
Elements						Sulfates
Cu cub. 7.05	Ag cub. 10.13	Mg hex. 13.8				FeSO <sub>4</sub> monocl. 45.0
Chlorides						Acetates
NiCl <sub>2</sub> trig.	FeCl <sub>2</sub> trig.	MnCl <sub>2</sub> trig.	FeCl <sub>2</sub> trig.	ZnCl <sub>2</sub> trig.		Zn(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> monocl.
		MgCl <sub>2</sub> type		MgCl <sub>2</sub> type		
36.3	39.5	41.1	39.5	45.8		
		AsI <sub>3</sub> type 55.1				

#### *Promoters for Palladium Catalyst*

Catalyst: Pd cub. 8.79
Promoters:
Elements
Mg hex. 13.8

#### *Promoters for Silver Catalysts*

Catalyst:	Ag cub.	Catalyst:	Ag <sub>2</sub> O cub. Cu <sub>2</sub> O type 31.6
Promoters:	10.13	Promoters:	
Elements			
Cu. cub. 7.05		Ni(OH) <sub>2</sub> amorphous 51.15	Cd(OH) <sub>2</sub> amorphous 57.3
			Mg(OH) <sub>2</sub> hex. 58.4

#### *Promoters for Rhenium Catalyst*

Catalyst:	Rh
	cub.
	8.24
Promoters:	
Elements	
Cu	Ag
cub.	cub.
7.05	10.13

Table 6.

## Poisons

Elements															
B	Cu	Mn	O	As	Hg	S	P	Se	Cl	Pb	Sb	Br	Te	Bi	I <sub>2</sub>
hex.	cub.	cub.	poly- morph.	trig. As type	hex.	rhomb.	trig. As type	trig. Se type	16.3	cub.	trig. As type	19.2	trig. Se type	trig. As type	rhomb.
3.25	7.05	7.26	10.9	13.0	13.7	15.0	15.4	15.8	16.3	17.9	18.1	19.2	20.2	21.0	24.5
Hydrides															
Al <sub>2</sub> O <sub>3</sub>	SO <sub>2</sub>	As <sub>2</sub> O <sub>3</sub>	CH : CH	H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te	HCN	PH <sub>3</sub>	AsH <sub>3</sub>	SbH <sub>3</sub>				
trig.		cub.	CH : CH <td>hex.</td> <td>cub.</td> <td>cub.</td> <td>cub.</td> <td></td> <td></td> <td></td> <td></td> <td colspan="4"></td>	hex.	cub.	cub.	cub.								
Corundum		Senarmonite	CH : CH <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>Phosphine</td> <td></td> <td colspan="4"></td>							Phosphine					
type		type								type					
25.7	32.6	50		19.3	26.9	30	~37		35	38					
Organic Compounds															
NiSO <sub>4</sub>	FeSO <sub>4</sub>	CO	CO <sub>2</sub>	CS <sub>2</sub>	CHCl <sub>3</sub>	Zn(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> OH								
rhomb.	rhomb.	trig.				monocl.									
43.0	45.0														
Sulfates															
Carbon dioxide	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH
trig.															
27															
														</	



*Poisons for Iron Catalyst*

Catalyst: Fe  
cub.  
7.05

Poisons:

Elements				
B	Ni	O <sub>2</sub>	As	P
hex.	cub.	hex.	hex.	hex.
3.25	6.55	10.9	13.0	15.41
			rhomb.	
			15.0	
Se	Te	Bi		
monocl.	hex.	hex.		
15.8	20.2	21.0		

Oxides

Ions  
Fe<sup>+++</sup>

H<sub>2</sub>O

Organic Compounds

Naphthalene

Catalyst: Fe (noble metal alloy)

cub.  
7.05

Poisons: O<sub>2</sub>  
polymorph.  
10.9

*Poisons for Nickel Catalyst*

Catalyst: Ni  
cub.  
6.55

Poisons:

Elements				
Cu	Mn	O <sub>2</sub>	As	Pb
cub.	cub.	hex.	hex.	cub.
7.05	7.26	10.9	13.0	17.9

Sulfates

SO<sub>2</sub>  
hex.  
27

Oxides

SO<sub>3</sub>  
rhomb.  
32.6

Organic Compounds

Thiophene

Catalyst: Ni (noble metal alloy)

cub.  
6.55

Poisons: O<sub>2</sub>  
polymorph.  
10.9

*Poisons for Copper Catalyst*

Catalyst: Cu  
cub.  
7.05

Poisons:

Elements	
Cu <sup>+</sup>	O <sub>2</sub>
cub.	polymorph.
7.05	10.9

† At moderate temperature

Organic Compounds

Thiophene

Catalyst: 60% MnO<sub>2</sub> + 40% CuO  
tetrag.  
17.0  
monocl.  
12.0

Poisons: CO<sub>2</sub>  
25.9



Tables 3, 4 and 5 refer to promoters specific for single catalysts used in the form of pure metals or their salts. Table 3 indicates promoters for nickel, nickel monoxide and nickel hydride, and for cobalt and cobaltous oxide catalysts. Table 4 contains promoters for copper, cupric oxide and cupric sulfate, as well as for iron, ferrous oxide, ferric oxide and ferrous sulfate catalysts. Table 5 lists promoters for platinum, platinum (ous) oxide, platinum (ous) oxide-platinum black, and palladium, silver, silver oxide and rhenium catalysts. These tables point to the fact that in many cases the promoter chosen has been isomorphous with the catalyst promoted; this was the case especially when elements or oxides were used as promoters. Oxide promoters serve as such for the metal as well as for its oxide-catalyst. These tables show how specific promoters are with regard to the kind of catalyst they promote.

Table 6 presents a list of poisons, the majority belonging to a group of elements, followed by their hydrides and organic compounds; less frequent poisons are recorded among the oxides, sulfates, chlorides, iodides, cyanides and arsenates. With the exception of such elements as copper, manganese and bismuth which, under certain conditions, may serve as promoters and therefore are not specific poisons and which occur either in a cubic or tetragonal or trigonal system, the poisons most frequently are of a trigonal or rhombic system similar to the inhibitors. Tables 7 and 8 list poisons found specific for various catalysts. Table 7 contains poisons for the catalysts platinum, platinum black, colloidal platinum, as well as for iron, nickel and copper. Table 8 contains poisons for the catalysts palladium, colloidal palladium, silver, tungsten and vanadium.

Tables 9, 10, 11, 12 and 13 show promoters and poisons specific for

Table 8.

<i>Poisons for Palladium Catalyst</i>		<i>Poisons for Silver Catalyst</i>	
Catalyst: Pd cub. 8.79	Catalyst: Colloidal Pd	Catalyst: Ag cub. 10.13	
Poison:	Poison:	Poison:	
Elements	Elements	Elements	
Hg hex. 13.7	Hg hex. 13.7	O <sub>2</sub> rhomb. (0.001 mm. skin) 10.9	
Hydrides			
H <sub>2</sub> S cub. 26.9			
Organic Compounds			
CO Traces of fatty vapors trig. 27			
		<i>Poisons for Tungsten Catalyst</i>	
		Catalyst: W cub. 9.50	
		Poison:	
		Elements	
		O <sub>2</sub> rhomb. 10.9	S rhomb. 15.0
		<i>Poisons for Vanadium Catalyst</i>	
		Catalyst: V cub. 8.2	
		Poison:	
		Elements	Oxides
		S rhomb. 15.0	As <sub>2</sub> O <sub>3</sub> cub. 50

catalytic reactions involving the same compound, so that a comparison and the evaluation of the influence of the type of reaction is possible.

Table 9 shows promoters and poisons for the synthesis, decomposition and oxidation of ammonia. Table 10 gives promoters and poisons for the decomposition and hydrogenation of hydrogen peroxide. In table 11 are tabulated promoters and poisons for the oxidation of sulfur dioxide and the hydrogenation of sodium sulfate. Table 12 shows promoters and poisons for the oxidation, reduction and hydrogenation of carbon monoxide. Table 13 contains promoters and poisons for the hydrogenation and dehydrogenation of methyl alcohol.

These tables should be consulted in the event of further systematic experimental study of the relationship between promoters, poisons and catalysts, or the type of catalytic reactions for which they are specific.

Table 9.  
Synthesis ( $\text{NH}_3$ )

Promoters				Poisons					
Promoter				Poison					
Ce cub. 20.2	Ca cub. 25.6	Sr cub. 33.2	Ba cub. 37.3	B hex. 3.25	As hex. 13.0	S rhomb. 15.0	P hex. 15.4	Se monocl. 15.8	Te hex. 20.2
Catalyst				Catalyst					
Fe cub. 7.05		Mo cub. 9.37		Fe cub. 7.05					
Promoter				Poison					
BeO hex. 8.3	MgO cub. 11.3	Al <sub>2</sub> O <sub>3</sub> hex. 25.7	K <sub>2</sub> O cub. 40	H <sub>2</sub> O hex. 19.3		PH <sub>3</sub> 35			
Catalyst				Catalyst					
Fe <sub>3</sub> O <sub>4</sub> Spinel type 44.5				Pt cub. 9.04					

#### Decomposition ( $\text{NH}_3$ )

Poison:	O <sub>2</sub> polym. 10.9	CO hex. 27	H <sub>2</sub> O (vapor) hex. 19.3
Catalyst:	Fe cub. 7.05		

#### Oxidation ( $\text{NH}_3$ )

Promoter:	(ThO <sub>2</sub> + CeO <sub>2</sub> ) or Bi						Poison:	PH <sub>3</sub>	H <sub>2</sub> S
Catalyst:	Fe <sub>2</sub> O <sub>3</sub>						Catalyst:	Pt gauze	
Promoter:	Tl	Pb	or their compounds				Poison:	O <sub>2</sub>	
Catalyst:	Fe						Catalyst:	Fe	
Promoter:	Cu	Ag	W	Bi	Th	Ce	Poison:	0.08–0.64%	H <sub>2</sub> O (vapor)
Catalyst:	Fe						Catalyst:	Fe	Al <sub>2</sub> O <sub>3</sub>
Promoter:	Bi <sub>2</sub> O <sub>3</sub>		CeO <sub>2</sub>		ThO <sub>2</sub>		Poison:	Bi	
Catalyst:	Fe						Catalyst:	Fe	
Promoter:	ZrO <sub>2</sub>		Bi <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO				
Catalyst:	CoO								

Since the data available are insufficient to justify any generalization, the above must be considered as the outline of a plan to be applied in future investigations concerning the problem of promoters and poisons.

(Text continued on page 423)

Table 10.  
Decomposition ( $\text{H}_2\text{O}_2$ )  
*Promoters*

Promoter: Glass wool	Promoter: $\text{CeCl}_3$ cub. 61.9	$\text{MnCl}_2$ hex. 41.1	$\text{NiCl}_2$ hex. 36.3	$\text{CoCl}_2$ hex. 38.1	Mn salts
Catalyst: Heavy metals	Catalyst: $\text{K}_2\text{Cr}_2\text{O}_7$				
Promoter: $\text{CuSO}_4$ tricl. 44.5	Promoter: $\text{Ni}(\text{OH})_2$	$\text{Cd}(\text{OH})_2$	$\text{Mg}(\text{OH})_2$		
Catalyst: Fe cub. 7.05	Catalyst: 51.15 $\text{Ag}_2\text{O}$ cub. 31.6	57.3	58.4		
Promoter: CuO tricl. 12.0	Promoter: $\text{FeSO}_4$ monocl. 45	$\text{CuSO}_4$ tricl. 44.5			
Catalyst: $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{Fe}(\text{OH})_3$	Catalyst: $\text{CuSO}_4$ tricl.	$\text{FeSO}_4$ monocl.			
	$\text{Fe}_2\text{O}_3$ cub. 30.3	44.5	45		
Promoter: $\text{Fe}(\text{OH})_3$					
Catalyst: $\text{Cu}(\text{OH})_2$					

*Poisons*

Poison: Hg hex. 13.7	HCN	$\text{I}_2$ rhomb. 24.5
Catalyst: Pt cub. 9.03		

Table 11.  
Oxidation ( $\text{SO}_2$ )

<i>Promoters</i>	<i>Poisons</i>			<i>Inhibitors</i>	
Promoter: BaO cub. 25.7	Poison: S rhomb. 15.0	As trig. 13.0	$\text{As}_2\text{O}_3$ cub. 50	Inhibitor: $\text{SO}_3$ 33.5	As trig. 13.0
Catalyst: V cub. 8.2	Catalyst: Pt cub. 9.03			Catalyst: Pt cub. 9.03	
	Poison: $\text{As}_2\text{O}_3$ cub. 50				
	Catalyst: V cub. 8.2				
	<b>Hydrogenation (<math>\text{Na}_2\text{SO}_4</math>)</b>				
Promoter: $\text{Ca}_3(\text{PO}_4)_2$ 99.3	Poison: $\text{H}_2\text{S}$ cub. 30	$\text{PH}_3$ 35			
Catalyst: Ni cub. 6.55	Catalyst: Ni cub. 6.55				

Table 12.

Oxidation (CO)				Poisons	
Promoters					
Promoter:	BeO	UO <sub>2</sub>	ThO <sub>2</sub>	Poison:	CO <sub>2</sub>
	hex.	cub.	cub.		CO <sub>2</sub> type
	8.3	24.8	26.4		25.9
	Cr <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> O <sub>3</sub>		Catalyst:	60% MnO <sub>2</sub> + 40% CuO
	hex.			Poison:	H <sub>2</sub> O (in high conc.)
	29.0	39.2		Catalyst:	Metals
Catalyst:	Co	Fe			
	hex.	cub.			
	6.58	7.05			
Promoter:	MnO <sub>2</sub> + CuO				
	Hopcalite				
Catalyst:	MnO <sub>2</sub> or	CuO			
	tetrag.	tricl.			
	17.0	12.0			
Promoter:	Ce				
	cub.				
	20.2				
Catalyst:	Ni				
	cub.				
	6.55				
Promoter:	Cr <sub>2</sub> O <sub>3</sub>				
	hex.				
	47.9				
Catalyst:	(MnO <sub>2</sub> + CuO)				

## Reduction (CO)

Promoter:	CeO <sub>2</sub>	ThO <sub>2</sub>		
	cub.	cub.		
	23.9	26.4		
Catalyst:	Ni			
	cub.			
	6.55			
Promoter:	BeO	ZrO <sub>2</sub>	CeO <sub>2</sub>	ThO <sub>2</sub>
	hex.	cub.	cub.	cub.
	8.3	22.0	23.9	26.4
	MoO <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>
	tetr.	cub.	hex.	hex.
	20.0	22.7	25.7	29.0
Catalyst:	Fe, Ni (various metals)			

## Hydrogenation (CO)

Promoter:	BeO	CeO <sub>2</sub>	ThO <sub>2</sub>	SiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	Poison:	CO (below 180°)
	hex.	cub.	cub.	cub.	hex.		
	8.3	23.9	26.4	22.7	29.0		
Catalyst:	Ni					Catalyst:	Ni
	cub.						
	6.55						

Table 13.

Hydrogenation (CH<sub>3</sub>OH)

Promoters		Poisons	
Promoter:	MgCO <sub>3</sub> (200°)	Poison:	Cu (at moderate temperature)
	hex.		cub.
	27.3		7.05
Catalyst:	Cu	Catalyst:	Cu
	cub.		cub.
	7.05		7.05

Dehydrogenation (CH<sub>3</sub>OH)

Promoter:	Th	Ce	Poison:	HgI <sub>2</sub>				
	cub.	cub.		tetrag.				
	19.7	20.2		69.8				
Catalyst:	Cu		Catalyst:	Pt				
	cub.			cub.				
	7.05			9.03				
			Poison:	S	Cl	Br	CHCl <sub>3</sub>	CS <sub>2</sub>
				rhomb.				
				15.0	16.3	19.2	36.1	45
			Catalyst:	Pt				
				cub.				
				9.03				





Table 16.  
*Promoters (Melting Points).*

Elements													
Bi	Tl	Ce	Mg	Sr	Ca	Ba	Ag	Cu	Mn	Ni	Co	Fe	W
271°	360°	640°	651°	752°	810°	850°	960.5°	1083°	1260°	1452°	1480°	1535°	3370°
Oxides													
Ag <sub>2</sub> O	NiO	CoO	CuO	FeO	ZnO	BaO	BaO	CaO	MgO	MnO <sub>2</sub>	CrO <sub>3</sub>		
300°	400°	800°	1026°	1420°	>1800°	1923°	2570°	2372°	2800°	-0535°	196°		
		decomp.	decomp.										
Ce <sub>2</sub> O <sub>3</sub>	PbO <sub>2</sub>	OsO <sub>3</sub>	Bi <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CeO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	UO <sub>2</sub>	ZrO <sub>2</sub>	ThO <sub>2</sub>			
200°	290°	650°	704-800°	1565°	1713°	1950°	1990°	2176°	2700°	>2800°			
ign.	decomp.	decomp.											
Chlorides													
AlCl <sub>3</sub>		SnCl <sub>4</sub>	ZnCl <sub>2</sub>	MnCl <sub>2</sub>	MgCl <sub>2</sub>	CeCl <sub>3</sub>	KF						
190° (25 atm.)		246°	262°	650°	712°	848°	880°						
Sulfates													
CuSO <sub>4</sub>	FeSO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	SrSO <sub>4</sub>	BaSO <sub>4</sub>									
+0.200°	64°	500-884°	1580°	1580° decomp.									

*Poisons (Melting Points).*

Elements													
Br	Hg		Cl	O	P(Y)	Se*	S	I <sub>2</sub>	Set	Bi	Pb	P(R)	Sb
-7.3°	-38.89°		-102°	-218.4°	44.1°	40-50°	112.8°	114°	200°	271°	327.4°	590°	630°
Oxides													
SO <sub>2</sub>	As <sub>2</sub> O <sub>3</sub>				Al <sub>2</sub> O <sub>3</sub>		H <sub>2</sub> Te	H <sub>2</sub> S	H <sub>2</sub> Se	AsH <sub>3</sub>	SbH <sub>3</sub>	HCN	
-72.7°	193° subl.				300° decomp.		-48°	82.9°	-88°	-113.5°	-88°	-14°	
Hydrides													
Organic Compounds													
							Thiophene	CO <sub>2</sub>		CHCl <sub>3</sub>	CS <sub>2</sub>	CO	
							-40°	-56.6° (5.2 atm.)		-63.5	-108.6°	-213°	

\* Amorphous

† Metallic

Cu 1083°  
Mn 1260°  
B 2300°  
HgCl<sub>2</sub> 275°

As 814° (36 atm.)  
Sulfates  
NiSO<sub>4</sub> -53.3°

Halides  
HgI<sub>2</sub> 130°





Table 18.  
*Promoters and Poisons in the Electromotive Force Series of Elements.*

Sr... 2.92	Ba... 2.90	Ca... 2.87	Mg... 2.40	Al... 1.70	Mn... 1.10	Te'' 0.827	Cd' 0.557	S'' 0.51	Fe... 0.441	Tl 0.330	Co... 0.278	Ni... 0.231	Sn... 0.136	Pb... 0.122
Fe... 0.045	H 0.000	Sb... -0.10	Bi... -0.226	As... -0.30	Cu... -0.344	O'' -0.397	Cu... -0.470	I' -0.534	Te... -0.558	Ag -0.7978	Hg -0.7986	Br' -1.065	Cl' -1.3583	
<i>Promoters (Valence).</i>														
Ag 1	Mg 2	Ca 2	Sr 2	Ba 2	Th 4	W 6	Cu 1,2	Tl 1,3	Ni 2,3	Co 2,3	Ce 3,4	Bi 3,5	Cr 2,3,6	Mn 2,4,6,7
O 2	B 3	Cu 1,2	Hg 1,2	Pb 2,4	As 3,5	P 3,5	Sb 3,5	Bi 3,5	S 2,4,6	Se 2,4,6	Te 2,4,6	Cl 1,3,5,7	Br 1,3,5,7	I... 1,3,5,7
<i>Promoters (Number of Electrons given off by Ionization).</i>														
Ag... -1	Mg... -2	Ca... -2	Cr... -2	Mn... -2	Fe... -2	Co... -2	Ni... -2	Cu... -2	Sr... -2	Ba... -2	Mn... -3	Fe... -3	Bi... -3	Th... -4
<i>Poisons (Number of Electrons given off by Ionization).</i>														
Cl' +1	Br' +1	I' +1	O'' +2	S'' +2	Mn... -2	Cu... -2	Hg -2	Pb -2	B... -3	Mn... -3	As... -3	Sb... -3	Bi... -3	Te... -4

Table 19.  
*Promoters (Arrangement of Electrons in Orbits for Atoms).*

Z	Shell	K	L			M			N			O			P	Q		
	Orbit	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	6s	6p	6d	7s
12	Mg	2	2	6	2	6		2										
20	Ca	2	2	6	2	6	5	1										
24	Cr	2	2	6	2	6	5	2										
25	Mn	2	2	6	2	6	6	2										
26	Fe	2	2	6	2	6	6	2										
27	Co	2	2	6	2	6	7	2										
28	Ni	2	2	6	2	6	8	2										
29	Cu	2	2	6	2	6	10	1										
30	Zn	2	2	6	2	6	10	2	6									
37	Rb	2	2	6	2	6	10	2	6	10								
56	Ba	2	2	6	2	6	10	2	6	10	1		6					
58	Ce	2	2	6	2	6	10	2	6	10	14		6					
74	W	2	2	6	2	6	10	2	6	10	14		6	4				
81	Tl	2	2	6	2	6	10	2	6	10	14		6	10				
83	Bi	2	2	6	2	6	10	2	6	10	14		6	10				
90	Th	2	2	6	2	6	10	2	6	10	14		6	10			2	

*Promoters (Arrangement of Electrons in Orbits for Ions).*

Shell	K	L	M	N	O	P	Q										
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	6s	6p	6d	7s
10 Mg..	2	2	4	2	4												
18 Ca..	2	2	4	2	4	3											
21 Cr...	2	2	4	2	4	4											
22 Cr...	2	2	4	2	4	4											
22 Mn...	2	2	4	2	4	4											
22 Mn...	2	2	4	2	4	4											
23 Mn...	2	2	4	2	4	5											
23 Fe...	2	2	4	2	4	5											
24 Fe...	2	2	4	2	4	6											
24 Fe...	2	2	4	2	4	6											
25 Co...	2	2	4	2	4	7											
25 Ni...	2	2	4	2	4	8											
27 Cu...	2	2	4	2	4	9											
36 Ag...	2	2	4	2	4	4+6	2	4	4+6								
40 Zn...	2	2	4	2	4	4+6	2	4	4+6								
49 Ba...	2	2	4	2	4	4+6	2	4	4+6								
54 Ba...	2	2	4	2	4	4+6	2	4	4+6	1							
55 Ce...	2	2	4	2	4	4+6	2	4	4+6	8							
78 Pt...	2	2	4	2	4	4+6	2	4	4+6	6+8							
80 Bi...	2	2	4	2	4	4+6	2	4	4+6	6+8							
86 Th...	2	2	4	2	4	4+6	2	4	4+6	6+8							
													4+6	2			
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													4+6	2			



Promoters and poisons no doubt owe their contrasting effect with regard to the catalyst to a difference in certain specific physico-chemical properties. *A priori*, a sharp difference in their characteristics would be expected because their actions are diametrically opposite.

Table 14 shows the distribution of promoters and poisons (elements) in the Mendeleeff Periodic System of Elements and their relation to definite chemical families differentiated by Mendeleeff. Elements enclosed in a striped frame compose groups of poisons in contrast to those in a plain frame, which designate a promoter family. The elements underlined correspond to elements not specific either for promoters or poisons, *i.e.*, able to play the part of either one, depending upon conditions or the type of catalytic reaction. Among properties indicating a contrast between promoters and poisons are considered the following: atomic volume ( $\frac{\text{atomic weight}}{\text{specific gravity}}$ ), boiling point and heat of vaporization (for poisons), Table 15; melting points, Table 16; and magnetic susceptibility, Table 17; electrical properties reflected in the position of promoters and poisons in the electromotive force series of elements, valence of both classes and number of electrons given off by ionization, Table 18; electronic configuration (arrangement of electrons according to quantum mechanics in orbits for atoms and ions) of promoters and poisons, Tables 19 and 20.

The comparison of atomic volumes for promoters and poisons classifies them into the chemical families mentioned above. While promoters are characterized by rather high boiling points, the specific poisons have on the average rather low boiling points. Poisons are also distinguished by a rather low heat of vaporization. Promoters are elements or compounds having a high melting point; poisons show a low melting point. The typical promoters are rather paramagnetic or slightly diamagnetic, while poisons are predominantly high in diamagnetism.

Promoters and poisons are distinctly divided into positively and negatively charged elements with respect to their place in the electromotive force series of elements. Thus it should be expected that both the promotion and poisoning effects would be expressed in a displacement of the electrochemical potential.\* Concerning the valence of promoters and poisons (elements), it seems that poisons are generally elements exhibiting different valences. In other words, they are more apt for transitions than the promoters. Promoters are elements only giving off electrons by ionization, while among poisons are also elements that may require electrons by the transition from the atomic state into the ionic state as established through tables of electronic configurations for promoters and poisons.

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\* Kaeb<sup>67</sup> stated that the electrochemical potential of poisoned platinum black is more noble than that of catalytically active. His findings show that the potential displacement varied between values of 3 millivolts (gas charge) and 200 millivolts (corresponding to inorganic salts); actually, the reverse effect should be expected.

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## Chapter 7

### The Role of Carriers in Heterogeneous Catalysis

Industrial practice emphasizes the significance of carriers as supports for catalysts in certain types of catalytic processes. In general by the term "carrier" is meant an inert material which acts as a support for the catalyst. When the so-called "carrier" increases or decreases the rate of the reaction, or directs the latter, it is no longer a carrier.

#### Functions and Mechanism of the Action of a Carrier

The function of a carrier with respect to the catalyst varies for individual cases. A carrier may be used to yield a cheaper substitute for the unexposed mass of an expensive catalyst, such as platinum, palladium, osmium, etc. Experimental data point to the fact that there is always a comparatively large mass of the catalyst which does not take part in the reaction. The thickness of the layer actually active has been estimated to be of the order of 200 to 300 mm. A carrier may be useful because it provides a larger contact surface and, at the same time, a more equal distribution of the catalyst.<sup>90, 105</sup> A carrier influences the structural and physical properties of the catalyst deposited on it. By preventing recrystallization, or baking together, a carrier preserves the fine dispersion of the catalyst and hinders aggregation which otherwise would occur.<sup>62, 93</sup> A carrier counteracts the decrease of the volume of a metal catalyst at high temperatures and prevents loss of catalytic activity.<sup>11</sup> A carrier may influence indirectly the activity of a catalyst by protecting it from poisons.<sup>45a</sup> It is believed that a carrier exerts a distorting action on the electric fields of the catalyst's active centers, changing thereby their sorptive ability and rendering them less sensitive toward catalyst poisons. It has been found<sup>8</sup> that the poisoning of platinum used in the oxidation of sulfur dioxide by arsenic pentoxide is weaker when platinum is precipitated on stannic oxide or zirconium oxide than when other carriers are used. In the poisoning of platinum by arsenous oxide, the latter is oxidized to the pentoxide, which accumulates at the active centers and destroys their catalytic effect. The degree of sensitivity of palladium toward catalyst poisons, such as arsenous oxide and carbon monoxide, in hydrogenation reactions depends to a great extent upon whether it is deposited on bone charcoal or kieselguhr (palladium on kieselguhr has less activity and a great sensitivity to poisons, whereas palladium on bone charcoal is more reactive, is not readily affected, and forms a stable catalyst). Therefore, activity and resistance to poisons may go hand in hand, but this is not always the case. Barium sulfate has proved to be a more favorably acting carrier than pumice, but is less stable toward poisons; a catalyst deposited on pumice appeared to be protected from the

action of poisons.<sup>88</sup> A carrier may also influence the adsorption, as well as increase the surface contact of the catalyst. Unless a certain concentration of active molecules is present on the catalyst surface and favorable conditions for activation exist, no catalytic reaction can take place. There are places of different activity<sup>82</sup> or centers of increased activity<sup>82</sup> on the catalyzing surface consisting of weakly attached atoms,<sup>42</sup> in which the reacting components are adsorbed exclusively.<sup>82</sup> The deciding factors for the activity of the catalyst surface are the distances between active points,<sup>19, 20a</sup> which are located on corners and edges of crystals. Since these points are isolated atoms or molecules, they are less saturated by bonds of neighboring atoms<sup>103</sup> than those located on the faces of crystals; therefore they are in a state of freedom which is necessary for the catalyzing action.<sup>12</sup>

The deposition of a catalyst on a carrier may amount to an increase in the number of active centers, corresponding to an energy level necessary to carry out a particular reaction. The form and magnitude of the electric field of the active centers has been considered very important.<sup>1</sup>

The superimposition of the electric field of the carrier and of the catalyst, which Willstätter calls "synergy," causes a change in the value as well as in the sign of the surface potential. The fact that insignificant amounts of a metal precipitated on the surface of charcoal changes its surface and adsorption properties has been noted by Frumkin.<sup>40</sup> He found that one atom of platinum per 10,000 surface atoms of charcoal induces the latter to change its charge in a hydrogen atmosphere. A platinized charcoal in a hydrogen atmosphere acts as a hydrogen electrode, disperses H ions into the solution and becomes negatively charged, thereby attracting cations from the solution (adsorption of alkalis). The same platinized charcoal in an atmosphere of oxygen or air behaves as an oxygen electrode, giving off OH ions into the solution and absorbing H ions; the surface, becoming positively charged, attracts anions from the solution (adsorption of acids). Taking into consideration Frumkin's theory, Adadurow and his co-workers assumed that the catalyst when deposited on a carrier uses a part of its valence for this type of sorption, whereby the external field of the catalyst atoms is distorted and its voltage decreased. If there is a correspondence of fields between the catalyst deposited on the carrier and the catalyzed molecules, the effect is positive; otherwise the distortion may interfere with or completely destroy the activity of the catalyst when deposited on a carrier.<sup>7</sup>

The mechanism of a carrier in catalytic reactions with respect to the catalyst which it supports as suggested by Adadurow<sup>1, 2, 3, 4, 6, 7</sup> emphasizes the fact that a carrier is not at all an indifferent support for a catalyst,\* but that it produces a deforming action upon the atoms or molecules of the catalyst, polarizes them, and brings about a change in their external fields, thereby changing their catalytic properties. Adadurow assumed that molecules of the reacting substance in a catalytic process are converted primarily from a normal state into an active state in which their configuration undergoes an essential change. Regardless of whether the bonds are

\* Refer also to <sup>90a</sup>.

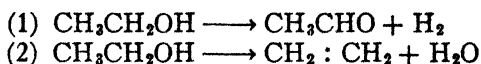


polar or non-polar, the atoms of molecules maintain a definite configuration under the influence of their superimposed electric fields. It is evident, however, that the electric field which combines atoms into one definite system must change in order that the configuration may change, and *vice versa*. In heterogeneous catalysis the electric field of the atom or molecule on the contact surface changes, depending upon whether the atom or molecule of the catalyst is attached to the lattice of the atom or molecule in the immediate vicinity, or to the lattice of a foreign body serving as its support or carrier. In the latter case, the atoms or molecules of the catalyst are subjected to the action of three types of forces: (a) attraction or repulsion forces (Coulomb forces); (b) forces of mutual polarization, and (c) forces of quantum mechanical resonance. The latter forces Adadurow considers as corresponding to a mutual action of the catalyst surface and the catalyzed molecules of the reacting substance. Under the influence of these forces of the acting surface of the carrier the catalyst is deformed or polarized and this causes a change in the external field of the catalyst on the carrier.

The laws<sup>110</sup> which determine the deformation or polarizability are: (a) the polarizability decreases with increase in the charge; (b) the polarizability decreases with a decrease in the volume of the ion, provided the charge is the same; (c) the deformability of the anion is considerably greater than that of the cation, and (d) the higher the charge and the smaller the radius of the deforming cation, the greater the influence of the deformed field of the cation; for equal charges the deforming influence is the stronger the smaller the radius of the cation.

According to Adadurow's conception of a catalytic process on a catalyst carrier, it is essentially the correspondence between the state of the electric field of the catalyst and that of the catalyzed reacting molecules. If the above-mentioned laws determining the deformation or polarization ability are applied for a particular carrier the influence of the carrier becomes greater with increasing radius and decreasing charge of the ion of the deposited catalyst, while for a particular catalyst the influence of the carrier is stronger the smaller the ion of the carrier and the greater its charge.

Adadurow's general conclusion concerning the choice of carriers states that they must be substances having a high deforming influence upon the atoms or molecules of the catalyst deposited on them. In order to meet this requirement, the ion of the carrier must possess the greatest possible charge and, at the same time, must have the smallest radius. The deformability of the catalyst must be high, and this is the case with ions of large atomic radii and small charge. The possibility of predicting the deforming or polarizing influence of carriers with respect to catalysts, as well as determining the conditions under which the greatest deforming influence may be exerted, was demonstrated by Adadurow in the mono-molecular decomposition of ethyl alcohol:



If two carriers are to be considered:

$$\begin{array}{l} \text{C} \quad r \sim 0.2 \text{ \AA} \\ \text{Si} \quad r \sim 0.39 \text{ \AA} \end{array}$$

then carbon, having the smallest radius and the same valence, as well as being catalytically inactive with respect to the reactant, alcohol, is to be preferred. As for the catalysts:

$$\begin{array}{l} \text{Cu} \quad 0.96 \text{ \AA} \\ \text{Al} \quad 1.33 \text{ \AA} \\ \text{Zn} \quad 1.49 \text{ \AA} \end{array}$$

the best deformation action of the three must be expected from zinc.

The effect of a support for a catalyst with respect to the catalytic reaction itself has been traced by Adadurow and his co-workers: (a) as a result of the distortion influence of the carrier, the activation energy of the catalytic reaction changes sharply; and (b) not only when a change in the sign of the potential of the catalyst is brought about by deposition on a carrier, but when the voltage of the field of active centers on the catalyst carrier is affected as well, then a change in the direction of the catalytic reaction may take place.

A change in the direction of the reaction itself may be brought about by choosing a suitable carrier for a catalyst<sup>7</sup> as illustrated by the dehydrogenation of ethyl alcohol on pure red copper,  $\text{CH}_3\text{CH}_2\text{OH} \longrightarrow \text{CH}_3\text{CHO} + \text{H}_2$ , which is converted into a dehydration reaction by depositing copper on birch charcoal,  $\text{CH}_3\text{CH}_2\text{OH} \longrightarrow \text{CH}_2 : \text{CH}_2 + \text{H}_2\text{O}$ .

Considering the rule<sup>13</sup> that in Volta's series: (+) Al, Zn, Sn, Cd, Pb, Sb, Bi, Hg, Fe, Cu, Au, Carbon, U, Pt, Pd,  $\text{MnO}_2$ ,  $\text{PbO}_2$  and other oxides (-), each member, when combined with a preceding member, becomes negatively charged, whereas, when combined with a succeeding member, it becomes positively charged, Adadurow deduced that on the surface of carbon through the deposition of copper a negative electric field is created, which induces changes in the properties of copper deposited on carbon.

Adadurow postulated that the deposition of copper on charcoal forms an unstable carbide, in which there is a displacement of the electric field and an outward action of copper atoms as a negative pole. Pure copper, like all metals, shows a positive valence. The negatively charged active centers of a copper catalyst precipitated on carbon repulse negatively charged hydrogen ions of hydrocarbons (Aston and Moers). A change in the sign of the potential when copper catalyst is supported on a carbon carrier prevents the catalyst from assisting in the dehydrogenation of alcohol and limits its activity to a dehydration reaction. Adadurow attempted to show further that a change in the direction of the catalytic reaction may be attained not only by a change in the electric field of the catalyst through deposition on a carrier, but also by a gradual change in the distortion of the field through a change in the amount of catalyst deposited on a carrier.

Zinc oxide is known to be a specific dehydrogenating catalyst, giving an aldehyde decomposition of ethyl alcohol. Bruckner's yield for the dehydro-

Precipitation of catalytic substances on carriers goes back as far as 1823 when Dobereiner first used a spiral of platinum wire and later potter's clay as a carrier for platinum black in his experiments on the behavior of

platinum black toward hydrogen, oxygen, carbon dioxide, ethylene, methane, etc.<sup>106</sup> The studies of Dulong, Thénard and Dobereiner indicate the use of substances in a fine state of dispersion and the application of inert substances, such as clay, asbestos, etc., as carriers. Clemens Winkler (Freiburg) obtained a patent [German P. 4,566 (1880)] in which he stated that carriers are true contact agents, *i.e.*, fluffy, porous substances such as asbestos, pumice, kieselguhr, clay, as well as fibrous materials such as cellulose, cotton, guncotton, etc. From this time in the development of catalysis, many other examples of the successful application of carriers in catalytic processes have been mentioned in the literature. These are referred to in Tables 2 to 13 inclusive.

(Text cont'd on page 449)

Table 2. Carriers in Synthetic Reactions.

Reaction	Catalyst	Carrier	Observer
Synthesis of water: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$	Metal.	Silica gel.	Sweeringen and Reyerson: <i>J. Phys. Chem.</i> , 32, 113-120 (1927); 32, 192-201 (1927).
Synthesis of water.	Pt.	Asbestos.	Emmett and Jones: <i>Ibid.</i> , 34, 1102-1104 (1930).
Synthesis of ammonia.	$\text{Ni}(\text{NO}_3)_2 + \text{Fe}(\text{NO}_3)_2 + \text{Al}(\text{NO}_3)_3$ , or an impregnating solution of 10% $\text{K}_2\text{CO}_3$ .	$\text{Si}(\text{OH})_4$ gel.	Marconi: Ital. P. 276,011, January 26, 1929.
Synthesis of ammonia. $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$	Alkali Fe cyanide.	Porous carrier.	Clancy: U.S.P. 1,363,393, December 28, 1930.
Synthesis of ammonia.	Fe, Os.	U containing N $\text{UN}_x + \text{N}_2 = \text{UN}_{(x+2)}$	Frankenburger: <i>Z. Elektr.</i> , 39, 818-820 (1933).
Synthesis of methane: $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	Ni + 10% Th.	Pumice.	
Synthesis of methane: $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ Temp., 300-400° Pressure, 10-20 atm.	Ni + Mn + Al mixed catalyst (most active and readily regenerated).	Kieselguhr or active charcoal.	Padovani and Franchetti: <i>Atti. Congr. Naz. Chim. pura Appl.</i> , 5, II, 818-828 (1936).
Synthesis of formaldehyde.	Mixture of oxides.	Pumice or asbestos.	
Synthesis of formaldehyde.	Mixture of oxides.	Quartz.	
Synthesis of formic acid from 69 p. CO and 25 p. water vapor at 325-900°; 50% theoretical yield.	Boron phosphate.	Wood charcoal.	E. I. Du Pont de Nemours & Co. (Vail): U.S.P. 1,895,238, January 24, 1933.
Preparation of propionic acid from ethylene; 72% CO, 3% $\text{C}_2\text{H}_4$ and 25% $\text{H}_2\text{O}$ vapor at 325° and 700 atm. pressure; 75% yield.	$\text{NH}_4\text{Cl}$ , $\text{NH}_4\text{Br}$ or $\text{NH}_4\text{I}$ ; 1% aqueous solution of $\text{NH}_4\text{Cl}$ .	Active carbon.	E. I. Du Pont de Nemours & Co. (Larson and Vail): U.S.P. 1,924,765, August 29, 1933.
Synthesis of propionic acid.	$\text{CaCl}_2$ or $\text{ZnCl}_2$ .	Active charcoal.	E. I. Du Pont de Nemours & Co. (Carpenter): U.S.P. 1,927,767, August 29, 1933.
Synthesis of propionic acid from ethylene at 325° temperature and 700 atm. pressure.	Inorganic volatile acids or halides.	Activated charcoal.	E. I. Du Pont de Nemours & Co.: U.S.P. 1,924,768, August 29, 1933.
Synthesis of trimethyl acetic acid: $(\text{CH}_3)_2\text{CH} \cdot \text{CH}_2\text{OH} + \text{CO} \rightarrow (\text{CH}_3)_2\text{C} \cdot \text{COOH}$ at 300° temp. and 700 atm. pressure.	Hydrogen halide.	Active charcoal.	E. I. Du Pont de Nemours & Co. (Larson): U.S.P. 1,995,930, March 26, 1934.

Table 2 (Continued).

Reaction	Catalyst	Carrier	Observer
Synthesis of methanol at 500-525°.	Sn phosphate: 20.0 g. SnCl <sub>4</sub> +11.7 g. 90% H <sub>3</sub> PO <sub>4</sub> .	20 g. large grained pumice (2 mm.).	Abkin and Medwedew: <i>Zh. Chim. Promysl.</i> , 11 (1) 30-34 (1934).
Synthesis of C <sub>2</sub> H <sub>5</sub> OH from olefins at 125-130° and under high pressure, 25 to 900 atm.	Volatile halides HCl, HI, HBr or CH <sub>3</sub> Cl, CCl <sub>4</sub> , NH <sub>4</sub> Cl	Pumice, silica gel, coke.	E. I. Du Pont de Nemours & Co.: U.S.P. 2,014,746, Sept. 17, 1935.
Synthesis of higher alcohols.	Pd.	Charcoal.	Commercial Solvents Corporation: G.P. 417,926, Cl 120, August 22, 1925.
Preparation of butanol from ethanol: CH <sub>3</sub> CH <sub>2</sub> OH + CH <sub>2</sub> =CH <sub>2</sub> → CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	Fe <sub>2</sub> O <sub>3</sub> +Al <sub>2</sub> O <sub>3</sub> activated by Yt, Zr, La.	Bone charcoal.	Dolgow and Wolnow: <i>Chim. Zh. obschtshei Khimii</i> , 3 (65) 313-318 (1933).
Preparation of acetone from acetic acid: CH <sub>3</sub> COOH + CO <sub>2</sub> + H <sub>2</sub> O → CH <sub>3</sub> COCH <sub>3</sub> + 2O <sub>2</sub>	(a) Cu, Al; (b) V, 2-A steel.	(a) Coal; (b) ceramic mass.	Deutsche Gold u. Silber Scheideanstalt (Roessler, Walter and Schultze): G.P. 581,047 Kl 120, July 20, 1933.
Preparation of ethyl ether of acetic acid from acetic acid and ethyl alcohol.	H <sub>3</sub> PtO <sub>4</sub> .	Pumice.	Backe, Roberts Co.: Brit. P. 131,088 (1918).
	TiO <sub>2</sub> , ThO <sub>2</sub> .	Active charcoal.	I. G. Farbenindustrie A.-G.: G.P. 434,279 (1924).
Synthesis of benzene: CO : H <sub>2</sub> = 1 : 1	Co-Th.	Kieselguhr.	Fischer and Koch: <i>Brennstoff-Chemie</i> , 13, 61-68, February 15, 1932.
Synthesis of benzene from CO and H <sub>2</sub> at ordinary pressure and at 210° temperature.	Co, Cu, Th, U in ratio 8 : 1 : 0.15 : 0.15; U exceeds Th in the polymerization action.	Starch (the catalysts + starch are highly porous).	Fujimura: <i>J. Soc. Chem. Ind. (Japan)</i> , 35, 179B-182B (1932).
Benzene synthesis from CO and H <sub>2</sub> over Co-Th-Mg catalysts.	Catalyst is highly active and may be readily regenerated; after extraction of the paraffin, catalyst washed out with cold water and CO <sub>2</sub> , whereby all Mg passes into solution as MgCO <sub>3</sub> ; basic salt in catalyst precipitated by heating the solution and blowing through vapor; remaining ingredients of the catalyst dissolved in HNO <sub>3</sub> , precipitated with NaOH, and the hot precipitate mixed again with the precipitated basic MgCO <sub>3</sub> .	MgCO <sub>3</sub> .	Ruhrchemie A.-G.: Ital. P. 349,478, March 31, 1937.
Benzene synthesis from water gas.	The catalyst is precipitated on a carrier, such as kieselguhr; from kieselguhr no damaging ingredients should pass into solution; such is often the case when used contacts are applied; therefore these ingredients must be first made insoluble, e.g., through glowing; furthermore, from the catalyst solution no damaging ingredients should be adsorbed on the carrier. Because of this, catalyst solutions must be used which do not contain such or have been previously eliminated by precipitation with alkali and separation of the precipitate.	Kieselguhr.	Ruhrchemie A.-G. (Roelen and Feisst): Austrian P. 103,630, May 5, 1938.

Table 3. Carriers in Decomposition Reactions.

Reaction	Catalyst	Carrier	Observer
Decomposition of $\text{H}_2\text{O}_2$ in an ammonia solution.	$\text{CuSO}_4$ (1.54 millimolar solution).	Glass wool.	Quartaroli: <i>Gazz. chim. ital. P.</i> , <b>61</b> , 466-78 (1931).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{MnO}_2$ .	Charcoal.	Roiter and Schafran: <i>Zhur. fizich. Chimii</i> , <b>4</b> , 461-464 (1933).
Decomposition of $\text{H}_2\text{O}_2$ at $400^\circ$ .	$\text{Fe}_2\text{O}_3$ or Pt sol.	Activated sugar charcoal.	Fowler and Walton: <i>Rec. trav. Chim.</i> , <b>54</b> (4), 476-480 (1935).
Thermal decomposition of $\text{Na}_2\text{SO}_4$ : 8-13% $\rightarrow \text{Na}_2\text{SO}_4$ : kaolin = 4 : 1 54-77% $\rightarrow \text{Na}_2\text{SO}_4$ : kaolin = 1 : 3 60% $\rightarrow \text{Na}_2\text{SO}_4$ on kieselguhr	$\text{CeO}_2$ , $\text{TiO}_2$ , $\text{Fe}_2\text{O}_3$ .	$\text{SiO}_2$ or kaolin.	Fialkow and Schargorodski: <i>Ukrain. Akad. Nauk. Sapsiski Institutu Chimii</i> , <b>2</b> , 269-283 (1935).
Decomposition of $\text{CaSO}_4$ by chlorine at $900$ to $950^\circ$ ; yield, 70%.	0.1 g. mol $\text{NiSO}_4$ to 1 mol $\text{CaSO}_4$ , using $\text{KCl}$ as a catalyst; lowest yield, 18.5%; $\text{NiSO}_4$ : $4\text{CaSO}_4$ : coal at $450-500^\circ$ yield, 1.3%; at $700-750^\circ$ , yield 96.2%.	Charcoal.	Budnikow and Krec: <i>Doklady, Acad. Nauk. U.S.S.R.</i> , <b>3</b> , 161-66 (1936).
Decomposition of methane: $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$	$\text{Fe}$ , $\text{Co}$ , $\text{Ni}$ .	Kaolin.	Nauss: G.P. 226,609 (1909).
Decomposition of methane.	$\text{Fe}$ , $\text{Co}$ , $\text{Ni}$ , $\text{Cu}$ .	$\text{MgO}$ or $\text{Al}_2\text{O}_3$ .	Badische Anilin u. Soda Fabrik: Russian P. 24,386 (1911).
Thermal decomposition of methane, using an electric discharge at a temperature of $1050^\circ$ ; $\text{C}_2\text{H}_2$ , 3.5%.	$\text{V}$ ( $\text{Mo}$ , $\text{Ni}$ ) coarse catalysts; $\text{Zr}$ ore, coke, active charcoal, kaolin.	Kieselguhr.	Kljukwin and Kljukwina: <i>Russ. Chimija tverdogo Topliva</i> , <b>6</b> , 130-146 (1935).
Decomposition of $\text{C}_2\text{H}_5\text{OH}$ .	$\text{Ni}$ .	Pumice.	Walker, Russel and Marschker: <i>J. phys. Chem.</i> , <b>34</b> , 2554-2566 (1930).
Decomposition of hydrocarbons with water vapor, $\text{CO}_2$ , $\text{O}_2$ , or air in $\text{H}_2$ - $\text{CO}$ or $\text{H}_2$ - $\text{CO}$ - $\text{N}_2$ mixtures.	Metal of the $\text{Fe}$ group.	Artificial $\text{Al}$ silicate or unburned natural $\text{Al}$ compound especially kaolin.	I. G. Farbenindustrie A.-G. (Wietzel and Hennicke): G.P. 554,551, Kl 12i, July 11, 1932.
Decomposition of aliphatic chlorides and bromides, e.g., propyl chloride, in gaseous phase.	$\text{H}_2\text{SO}_4$ , conc.	Pumice.	Senderens and Aboulene: <i>Compt. rend.</i> , <b>202</b> , 1548-1550 (1936).
Cracking of crude petroleum oil.	$\text{Fe}_2\text{O}_3$ , $\text{Ni}$ , $\text{NiO}$ .	Pumice or infusorial earth.	Osterstrom and Wagner: F.P. 654,782, April 10, 1929; Austrian P. 13,623, Jan. 22, 1929.
Splitting of hydrocarbon oils.	$\text{Ti}$ , $\text{Zr}$ , $\text{Th}$ , $\text{B}$ , $\text{Si}$ .	$\text{Fe}$ or not highly alloyed steels.	I. G. Farbenindustrie A. G.: G.P. 578,504, Kl 23b, June 14, 1933.
Splitting of aliphatic monobromine derivative $\text{C}_n\text{H}_{2n+1}\text{Br} \rightarrow \text{HBr} + \text{C}_n\text{H}_n$	$\text{ThO}_2$ , $\text{Al}_2\text{O}_3$ .	Kaolin.	Senderens: <i>Compt. rend.</i> , <b>200</b> , 2137-2139, June 24, 1935.
Splitting method by filtering through a contact at $150-300^\circ$ .	$\text{AlCl}_3$ ( $\text{ZnCl}_2$ , $\text{MgCl}_2$ , $\text{CuO}$ ).	Bauxite (activated through grinding with water and heating to a red glow).	Catalysts, Ltd. (Gifford): E.P. 445,727 and E.P. 445,757, May 14, 1936; F.P. 797,947, May 6, 1936.

Table 4. Carriers in Oxidation Reactions

Reaction	Catalyst	Carrier	Observer
Oxidation of: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	Pt.	Asbestos.	Petrie: Brit. P. 590 (1852). Winkler: G.P. 4,566 (1878).
Oxidation of: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	Pt.	Solid salts such as $\text{CuO}$ , $\text{Fe}_2\text{O}_3$ , or $\text{Cr}_2\text{O}_3$ , or $\text{CuO} + \text{Cr}_2\text{O}_3$ .	Grillo and Schroeder: G.P. 102,244 (1898).
Oxidation of: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	$\text{FeSO}_4$ .	Burned pyrite.	M.L.B.: G.P. 139,554 (1902).
Oxidation of: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	Pt.	$\text{Fe}_2\text{O}_3 \cdot \text{CuO}$ .	Badische Anilin u. Soda Fabrik: G.P. 291,792 (1913); Swiss P. 71,326 (1913).
Oxidation of: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	Pt, Os, or Ni.	Fibers.	G.P. 354,212, Kl 12g, June 1, 1922; F.P. 532,343, February 1, 1922.
Oxidation of: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	Pt sol.	$\text{MgSO}_4$ or porous ceramics.	Astner: E.P. 265,938, April 6, 1927.
Oxidation of: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	Pt.	Carrier.	G.P. 440,338, Kl 12i, December 2, 1927.
Oxidation of: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	$\text{V}_2\text{O}_5$ , $\text{MoO}_3$ , $\text{Cr}_2\text{O}_3$ , $\text{Mn}_2\text{O}_3$ , $\text{Mn}_2\text{O}_7$ , $\text{WO}_3$ .	Zeolites.	Selden Co.: U.S.P. 1,657,753, Jan. 31, 1928.
Oxidation of: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	One or more metals or their salts.	Many component zeolites prepared from silicates.	Selden Co.: E.P. 290,316, June 14, 1928.
Oxidation of: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	Catalyst.	Double zeolites.	Selden Co.: E.P. 296,048, October 17, 1928.
Oxidation of: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	Pt.	Silicic acid gel.	Holmes, Ramsay and Elder: <i>Ind. Eng. Chem.</i> , 21, 850-853 (1929).
Oxidation of: $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ ; temperature, 450°; yield, 97-98%.	Mn salts.	Water glass solution.	Chamadarjan and Brodowitsch: <i>Ukrain. Chem. J.</i> , 8, Part 2, 58-65 (1933).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ ; a gas of 6 to 7.5% $\text{SO}_2$ content in temperature interval 350-475°; yield 96-97% conversion; the efficiency of the method is 5.2 tons $\text{H}_2\text{SO}_4$ per K.	Pt.	The waste from $\text{AlCl}_3$ manufacture from kaolin according to Budnikoff's method.	Adadurow, Budnikoff and Rjabtschenkow: <i>Zhur. prikl. Chim.</i> , 7, 1147-1152 (1934).
Catalytic oxidation of $\text{SO}_2$ .	Pt (0.015-0.02%).	Al wire (2 mm. in diam., 3 mm. long), as well as other metallic carriers, Cr, Ni; (with ordinary Pt carriers, such as silica gel, the attainment of the ideal temperature course is impossible due to their small heat conductivity).	Adadurow, Zeitlin and Orlowa: <i>Ukrainski Chim. Sh.</i> , 10, 346-361 (1935).
Catalytic oxidation of $\text{SO}_2$ .	V (impregnated with $\text{KVO}_3$ ).	Silica gel.	Tschufarow, Tatijewakaja and Kulpina: <i>Zhur. fizich. Chim.</i> , 6, 152-156 (1935).

Table 4 (Continued).

Reaction	Catalyst	Carrier	Observer
Catalytic oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{NH}_4\text{VO}_3$ ; $\text{KVO}_3$ ; V sulfate.	$\text{Si}(\text{OH})_4$ ; 10-20 p. $\text{SiO}_2$ to 1 p. V; $[\text{Si}(\text{OH})_4]$ ppt. from alkali solution so that final solution is slightly alkaline or neutral to Congo red; the ppt. mixed to a paste with V compound and $\text{K}_2\text{SO}_4$ added; V : K = 1 : 2- $\frac{1}{2}$ up to 1 : 3- $\frac{1}{2}$ .	Calco Chemical Co., Inc.; U.S.P. 2,027,316, January 7, 1936.
Catalytic oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{NH}_4\text{VO}_3$ ; an alkali compound and gum arabic, or tragacanth, for example, 416 p. kieselguhr is heated to a red glow, mixed with 21 p. tragacanth to which has been added 50 p. $\text{NH}_4\text{VO}_3$ and 56 p. KOH.	Kieselguhr.	General Chemical Co.; U.S.P., 2,029,376, February 4, 1936.
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ .	(a) Thin layers of Pt and $\text{V}_2\text{O}_5$ ; (b) Cathodic dispersion of Pt or layer of Pt.	(a) glass; (b) iron surface.	Dankow, Joffe, Kotschetkow and Perewesentzew: <i>Zhur. Obshchei. Khim.</i> , <b>4</b> , 334-342 (1933).
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ .	Pt vapors condensed in a vacuum; the same activity as ordinary Pt on asbestos.	Asbestos.	Dankow, Joffe, Kotschetkow and Perewesentzew: <i>Ibid.</i> , <b>4</b> , 334-342 (1933).
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ .	Colloidal Pt impregnated in small amounts; Pt by reduction of $\text{PtCl}_4$ .	Silica gel; higher activity for colloidal Pt brought upon ready gel.	Charmadarian and Dachnjuk: <i>Ukrain Chim. J.</i> , <b>8</b> , Part 2, 36-43 (1933).
Oxidation of $\text{SO}_2$ (maximum yield at $550^\circ$ ). Activators: $\text{CuSO}_4$ , $\text{Fe}_2(\text{SO}_4)_3$ , $\text{BaCl}_2$ , $\text{MnSO}_4$ .	$\text{V}_2\text{O}_5$ (from $\text{NH}_4\text{VO}_3$ at $440^\circ$ ).	Asbestos; $\text{MnO}_2$ (best results) infusorial earth glass; porcelain quartz.	Charmadarian and Brodowitsch: <i>Zhur. Priklad. Khim.</i> , <b>7</b> , 725-28 (1934).
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ .	$\text{Ti}_2\text{O}_3$ : $\text{Ag}_2\text{O}$ : $\text{V}_2\text{O}_5$ = 1/4 : 1 : 1	Kieselguhr or diatomaceous earth or celite pieces; (250 vol. P silo-cel C 22).	Selden Co. (Fiedler and Jaeger); U.S.P. 1,945,267, January 30, 1934.
Manufacture of $\text{H}_2\text{SO}_4$ from 2% $\text{SO}_2$ activated at $350^\circ$ .	Pt; plating with Pt occurs with 0.1% $(\text{NH}_4)_2 \cdot \text{PtCl}_6$ solution.	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$ (grained mass, 2.5-3.5 mm.).	Mototaro Matski and Ken-ichi Oda: <i>J. Soc. Chem. Ind. Japan</i> , <b>38</b> , 148B-151B (1935).
Oxidation of: (1) $\text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ (2) $\text{H}_2\text{SO}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{SO}_5$	Vanadium.	$\text{K}_2\text{O} \cdot \text{VO}_2 \cdot \text{SiO}_2$ .	Metall A.-G. (Siecke and Koolmann): G.P. 610,448, Kl 12, March 13, 1935; G.P. 610,449 Kl 12, March 11, 1935.
Manufacture of $\text{H}_2\text{SO}_4$ .	Pt (0.01-0.5%); Pt may be substituted by Rh up to 10%; Pt ppt. only on the internal surface of the gel, while the external surface has as a coating free Pt containing less active substances than Pt in $\text{Fe}_2\text{O}_3$ or $\text{Cr}_2\text{O}_3$ .	$\text{SiO}_2$ gel.	American Platinum Works, F.P. 803,746, October 7, 1936.
Oxidation of $\text{NH}_3$ .	Pt, Os, or Ni.	Fibers.	G.P. 354,212, Cl 12g, June 1, 1922; F.P. 532,343, February 1, 1922.



Table 4 (Continued).

Reaction	Catalyst	Carrier	Observer
Oxidation of $\text{NH}_3$ .	Alkali.	Cr silicate.	G.P. 298,981, Cl 12i, June 16, 1926.
Oxidation of $\text{NH}_3$ .	Alkali.	V or B silicate.	
Oxidation of $\text{NH}_3$ : (1) $\text{NH}_3 + 2\text{O}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O}$ (2) $4\text{NH}_3 + 5\text{O}_2 \rightleftharpoons 4\text{NO} + 6\text{H}_2\text{O}$	Alkali or alkaline earth compounds.	Poly-zeolites.	G.P. 298,981, Cl 12i, June 16, 1926.
Oxidation of $\text{NH}_3$ .	HCl-Co.	W silicate.	E.P. 300,583 (1929).
Oxidation of $\text{NH}_3$ .	Pt.	Quartz.	Imperial Chemical Industries, Ltd. (Smyth); E.P. 346,800, May 14, 1931.
Oxidation of $\text{NH}_3$ .	Pt or Cr; Fe < Sr < U < Mn < Ce < Mo < W < Cr < (increase in activity according to this sequence).	Pozzuolana (a form of siliceous rock of volcanic origin).	G.P. 545,427, Kl 12i, February 29, 1932; Marmier: <i>Compt. rend. heb. Seance Acad. Sci.</i> , 199, 868-869 (1934).
Oxidation of $\text{NH}_3$ .	Mounted wire spiral of Cr steel or Pt metal or Pt-Rh.	"Celite" sticks (temperature, 1000-1500°).	Bayerische Stickstoffwerke A.-G.: F.P. 976,205, January 21, 1935.
Oxidation of $\text{NH}_3$ ; yield 95.5-99.1%.	Pt electroplated; 5-6% Pt of the weight of the Ni wire nets.	Ni wire gauzes; stability of gauze increases up to a certain degree, but does not prevent penetration of $\text{H}_2$ for a long time.	Adaduwor and Proskowski: <i>Zhur. Priklad. Khim.</i> , 8, 1321-1329 (1935).
Oxidation of CO.	CuO (pptd.).	Quartz or asbestos.	
Oxidation of CO: (1) $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ (2) $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$	Fe-containing substances.	Carrier.	Fourneau and Ribas: <i>Bull. Soc. Chim.</i> , 4 (39) 1587-1589 (1926).
Oxidation of CO.	$\text{MnO}_2$ (pure and free from Fe and heated in an oxidizing atmosphere).	$\text{MnO}_2$ adsorbed.	Mathieu-Levy: <i>Compt. rend.</i> , 196, 1319 1321, May 1, 1933.
Oxidation of CO.	Catalysts, adsorption cmpds; three stages of activity in the life of a catalyst, second stage important.	$\text{MnO}_2$ .	Mathieu-Levy and Geroso: <i>Bull. Soc. Chim. (A)</i> , 53, 1039 1050 (1933).
Oxidation of CO: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	$\text{FeCO}_3 + 0.7\% \text{ K}_2\text{Cr}_2\text{O}_7$ ; highly active at 500°; does not decompose as readily as pure siderite; CO alone highly active, but very unstable.	MgO (increases stability).	Iwanowsky, Braude and Panina: <i>Zhur. Khim. Prom.</i> , (2), 37-44 (1934).
Oxidation of CO: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	$\text{Fe}(\text{OH})_3$ mixed with $\text{Na}_2\text{CO}_3$ .	Dehydrating binding agent, e.g., cement (serves to solidify the catalyst); rotating drum used.	Non-Poisonous Gas Holding Co., Ltd.: F.P. 777,546, February 22, 1935.
Preparation of a gas free from CO or CO containing combustible gases; two stages in the process: (1) oxidation; (2) hydrogenation.	(1) $\text{Cr}_2\text{O}_3$ containing Fe. (2) Ni + $\text{ThO}_2$ .	Active charcoal. Active charcoal.	Kemmer: G.P. 617,565, Kl 20a, August 21, 1935.
$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$	Ni and Cu.	Fireproof material.	Tessig du Motay: U.S.P. 229,338 (1879). Mond and Langer: G.P. 51,572 (1889).

Table 4 (Continued).

Reaction	Catalyst	Carrier	Observer
$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	Ni(NiO).	MgO.	Badische Anilin u. Soda Fabrik: G.P. 296,866 (1912).
Oxidation of $\text{CH}_4$ : (1) $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ (2) $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$ (3) $2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 2\text{H}_2$	Ni, NiO, Ni + $\text{Al}_2\text{O}_3$	MgO.	Badische Anilin u. Soda Fabrik: G.F. 306,301 (1914).
$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	Metals.	Coke, carbon.	Cumberland Coal Power: Brit. P. 181,062 (1921).
Oxidation of methane to formaldehyde: $\text{CH}_4 \rightarrow \text{CH}_2(\text{OH})_2$ $\text{CH}_2(\text{OH})_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$	Mixture of oxides $\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$	Pumice, asbestos, or quartz.	Bakelite Co.: G.P. 411,215 (1927).
Incomplete oxidation of methane with oxygen or air at 850–950°; residue gas contains less than 1% $\text{CH}_4$ .	$\text{Ni}(\text{NO}_2)_2$ serves for impregnating.	Fireproof material.	Padovani and Franchetti: <i>J. Chim. Ind. App.</i> , 15, 429–432 (1933).
Oxidation of olefins to alcohols.	$\text{MnCO}_3$ , $\text{H}_3\text{BO}_3$ , $\text{H}_3\text{PO}_4$ .	Linseed oil (the mixture of linseed oil and catalyst is heated and pressed into tablets).	Distillers Co., Ltd. (Joshua, Stanley and Dymock): E.P. 404,115, February 1, 1934.
Oxidation of paraffins in a liquid phase.	$\text{CuSO}_4$ .	Pumice.	Schaal: G.P. 32,705 (1884).
Oxidation of organic compounds in gaseous state.	V, Mo, Ta, W, Cr, U, Mn, Bi, Fe, Co, Ni, Cu, Ag oxides singly or in mixtures.	Zeolites; double Al silicate natural zeolites, naphelite, lenite or feldspar.	Selden Co.: U.S.P. 1,694,122, December 4, 1928.
Oxidation of acetylene at 400–410°: (1) $\text{C}_2\text{H}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO}$ (2) $2\text{C}_2\text{H}_2 + 3\text{H}_2\text{O} \rightarrow \text{CH}_3\text{COCH}_3 + \text{CO}_2$ (3) $\text{C}_2\text{H}_2 + 2\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3\text{CH}(\text{OCOCH}_3)_2$	Fe free catalyst Zn acetate and Mn acetate.	Porous charcoal (200 g. coal + 35 g. Zn acetate + 10 g. Mn acetate).	Deutsche Gold u. Silber Scheideanstalt (Roessler, Walter and Schultz): G.P. 577,705 Kl 120, June 3, 1933.
Oxidation of acetylene to acetone.	Mixture of Zn or Cd. basic cmpds. as well as mixture of alkalis or alkaline earths.	Wood charcoal (highly active).	Deutsche Gold u. Silber Scheideanstalt (Roessler and Walter): G.P. 584,517, Kl 120, September 21, 1933.
Oxidation of acetaldehyde to acetic acid.	Pt.	Asbestos.	Dreyfus: F.P. 487,412 (1918).
Oxidation of acetaldehyde to acetone.	19% $\text{Al}_2\text{O}_3$ , 8.8% Ni tartrate.	Silica gel (by adding dilute $\text{NaNO}_3$ to purified silica xerogel, the yield of acetic acid is increased).	Ackermann and Burton: <i>Chem. Age</i> , 31, 169–170 (1934).
Oxidation of butyl aldehyde to butyric acid.	Mn butyrate.	Chamotte.	Legg and Adam: Brit. P. 173,004 (1920); U.S.P. 1,418,448 (1921).
Oxidation of methanol: $\text{CH}_3\text{OH} + 1/2\text{O}_2 \rightarrow \text{COH}_2 + \text{H}_2\text{O}$	Pt.	Asbestos.	M.L.B. (Trillat): G.P. 55,176 (1889).
Oxidation of methanol.	Ag.	Asbestos.	Blank: G.P. 228,697 (1908).

Table 4 (Continued).

Reaction	Catalyst	Carrier	Observer
Oxidation of methanol to formaldehyde: (1) 90% yield. (2) 92% yield.	(1) Ag. (2) Ag. (used for plating).	Pumice. Cu (wire net).	Gurewitsch and Tschirwinskaja: <i>Zhur. Khim. Prom.</i> , 12, (1) 57-61 (1935).
Oxidation of alcohol to acetic acid.	Light metals or Cu.	Pumice. Asbestos.	Bayer Co.: G.P. 346,520 (1917). Glock: G.P. 109,015 (1899).
Oxidation of $C_2H_5OH$ $CH_3CH_2OH + (O_2) \rightarrow$ $CH_3C(=O)H + H_2O$	Ag.	Charcoal, brown coal.	Demestedt and Hassler. G.P. 203,348 (1907). Goldschmidt: Brit. P. 290,523 (1927); U.S.P. 1,666,447 (1928). Holzverkohlung Industrie A.-G.: Brit. P. 294,037 (1927).
Oxidation of methanol to formaldehyde.	Impregnated with $AgNO_3$ (dried, treated with dilute formic acid).	Porous, inert material such as asbestos, porcelain.	Soc. An. Ch. Mildé Pils and Cie.: Swiss P. 169,857, September 17, 1934.
Oxidation of higher alcohols	$K_2PtCl_6$ acts negatively; $Na_2PtCl_6$ used for impregnating, reduced to Pt.	Asbestos.	Dabietos and Makris: <i>Praktika de l'Acad. d'Athens</i> , 3, 569 (1928).
Oxidation of benzene, phenol, furfural to maleic acid.	Oxides of Fe, Co, Ni, Cu, or Al, or $V_2O_5$ .	Non-exchangeable base: silicates, water glass.	Selden Co.: U.S.P. 1,811,363, March 29, 1932.
Oxidation of benzene to maleic acid (410-450°) main reaction: $2C_6H_6 + O_2 \rightarrow 2C_6H_5OH \xrightarrow{O_2} O = \langle \text{benzene ring} \rangle = O + 3O_2 \rightarrow$ $HOOC \cdot HC = CH \cdot COOH + 2CO_2$ side reaction: (with small amts. of maleic acid anhydride and formaldehyde) $C_6H_4O_2 + 2O_2 \rightarrow HC = CH + (CO)_2O + CH_2O + CO_2$	$V_2O_5$ .	Pumice or asbestos fibers.	Salkind and Solotarew: <i>Zhur. Priklad. Khim.</i> , 6, 681-684 (1933).
Oxidation of toluene to benzaldehyde to benzoic acid.	$H_3PO_4$ .	Pumice	Badische Anilin u. Soda Fabrik: G.P. 408,184 (1920).
Oxidation of toluene in a vapor phase.	Higher oxides of Mo or V in an acid solution with ferro-chromium together with non-reduced oxides.	Carrier.	Bogdanow and Leznov: Russ. P. 38,633, September 30, 1934.
Oxidation of toluene.	Fe vanadate and Fe oxide.	Asbestos fibers.	Adam, Shannon and Cockney (Gas, Light and Coke Co.).
Oxidation of naphthalene to phthalic anhydride.	V; 42 p. $K_2SiO_4$ , 70 p. zeolite, 18 p. $V_2O_5$ mixed and dissolved in conc. KOH then mixed with 5 p. $Al_2O_3$ in KOH (heated to 60°) + 10% $H_2SO_4$ added until viscous, filtered, dried (at 100°) and reduced to powder.	Artificial zeolites.	Selden Co.: U.S.P. 1,515,299 (1927). 1,599,228.
Oxidation of naphthalene.	Catalysts.	Zeolites.	Selden Co.: U.S.P. 1,692,126, November 20, 1928.

Table 4 (Continued).

Reaction	Catalyst	Carrier	Observer
Oxidation of naphthalene to the anhydride of phthalic acid.	35-75% $V_2O_5$ (from $NH_3$ ; metavanadate ppt. $V_2O_5$ by $HNO_3$ ); sucrose or glucose solution added; mixture heated, with elimination of water and combustion of the organic substance, as well as partial melting of $V_2O_5$ at 660-675°.	Inert non-melting carrier such as melted $Al_2O_3$ or $TiO_2$ .	E. I. Du Pont de Nemours & Co. (Calcott and Douglas): U.S.P. 2,034,896, March 24, 1936.
Oxidation of anthracene to anthraquinone.	$H_2VO_4$ .	Pumice.	Badische Anilin u. Soda Fabrik: G.P. 408,184 (1920).
Oxidation of anthracene (vapors) to anthraquinone by air (400°).	K vanadate and Cu or Ni compounds the basic radical of which is able to enter into the non-exchangeable nucleus of the zeolite.	At least one zeolite; reaction product of one silicate, such as Na silicate.	Selden Co. (Jaeger): U.S.P. 1,886,023, January 11, 1932.

Table 5. Carriers in Reduction Reactions.

Reaction	Catalyst	Carrier	Observer
Reduction of CO.	Ni.	Asbestos.	Pieters: <i>Chem. Weekblad</i> , 28, 209-210, March 28, 1931.
Reduction of CO at ordinary pressure.	Co:Cu:MgO in the ratio 3 : 1 : 0.45.	Pumice (better gas contraction; 60% obtained with coke).	Fujimura: <i>J. Soc. Chem. Ind. Japan</i> , 34, 227B-229B (1931).
Reduction of $CO_2$ at 150-200°: $CO_2 + C \rightarrow 2CO$	$Na_2CO_3$ .	Wood charcoal.	Edenholm and Widell: 4, A 1934, 26-39, April 1.
Reduction of oxygen-containing organic compounds.	Fe, Cr, or Ni.	Charcoal.	Handelsondernaming (Fenhald): G.P. 434,211, Cl 120, September 21, 1926.
Reduction of organic compounds.	Ni acetate (precipitate at low or moderate temperature).	Siloxen (oxydisilin).	G.P. 540,327, Kl 120, December 18, 1931; Add to G.P. 539,174, Kl 120, November 23, 1931.
Reduction of higher alcohols; primary and secondary alcohols obtained; at high pressure, hydrogenated to alcohols free from aldehydes and ketones.	Ni.	Kieselguhr, Cu chromite, Cu-Ba chromite.	Morgan, Douglas and Hardy: <i>J. Soc. Chem. Ind.</i> , 52, 518-519 (1933).
Reduction of ketones (propiophenone in alcoholic solution).	Pd.	Bone charcoal.	Hartung and Crossley: <i>J. Am. Chem. Soc.</i> , 56, 158-169 (1934).
Reduction of primary amines of the benzene series.	Cu, Ag, Au.	Silica gel or $Al_2O_3$ gel.	I. G. Farbenindustrie, A.-G.: E.P. 295,824, September 13, 1928; E.P. 297,212, October 11, 1928.
Reduction of aromatic nitro compounds to amines by $H_2$ .	Ni nitrate activated by sulfides or chlorides mixed with metals (Ag, Cu, Fe), or difficultly reducible oxides $Al_2O_3$ ; $MgO$ , $Cr_2O_3$ , $ZnO$ ; silicic acid.	Kieselguhr or pumice.	Furakawa and Kubote: Japanese P. 101,254, July 5, 1933.

Table 6. Carriers in Hydrogenation Reactions.

Reaction	Catalyst	Carrier	Observer
Hydrogenation of organic compounds.	Pt.	Natural or artificial zeolites.	Mittasch, Schneider and Morawitz: U.S.P. 1,215,396, February 13, 1917.
Hydrogenation of unsaturated compounds.	Ni, Pd.	Al or pumice.	Lessing: Austrian P. 82,207, December 27, 1920.
Hydrogenation of $C_2H_4$ .	Pt (plated on wire).	Wire.	Tauber: <i>Z. phys. Chem. B</i> , <b>19</b> , 99-101 (1932).
Hydrogenation of $C_2H_4$ .	Ni.	Active wood charcoal.	Schuster: <i>Chem. Age</i> , <b>26</b> , 46, January 16, 1932.
Hydrogenation of $C_3H_2$ to $CH_4$ .	Pt or Cu.	Silica gel.	
Hydrogenation of $C_2H_2$ to $C_2H_4$ .	Pd.	Silica gel.	
Hydrogenation of olefins at 150-250°.	Th oxide or Pt, Au, Cu, W, or their compds.	Basic substances: wood charcoal, asbestos, pumice, active silica.	Dreyfus: E.P. 389,136, April 6, 1933.
Hydrogenation and dehydrogenation of organic compounds at 295-300°.	Pd.	Pd wire gauze.	Dow Chemical Co. (Bass) U.S.P. 1,907,710, May 9, 1933.
Hydrogenation of CO at atmospheric pressure.	Fe-Cu (precipitated from Fe and Cu nitrate solution).	Kieselguhr acts unfavorably.	Antheaume: <i>Ann. combustibles liquides</i> , <b>10</b> , 473-507, May-June (1935).
Hydrogenation of simple homologs of cyclopentane.	Pt.	Charcoal activated at 305-315°.	Zelinsky and Kasansky and Plates: <i>Ber.</i> , <b>68</b> , 1869-1872, September 11, 1935.
Hydrogenation of fatty acids and esters.	Ni.	Pumice.	Erdmann and Bedford: <i>Ber.</i> , <b>42</b> , 1324 (1909).
Hydrogenation of fatty acids.	20% Ni.	Kieselguhr.	Kailan and Stuber: <i>Monatsh.</i> , <b>62</b> , 90-100 (1932).
Hydrogenation of fatty acids.	$SiO_2$ , $Al_2O_3$ , $Ce_2O_3$ .	Talc, wood charcoal, bone charcoal.	
Hydrogenation of fatty acids at 180°.	Zn, Pb, Ag, Sb.	Kieselguhr.	
Hydrogenation of maleic and fumaric acids, and Na cinnamate.	Pd.	Blood, birch fungus, bone, sugar charcoal, $BaSO_4$ and kieselguhr.	Sabalitschka and Moses: <i>Ber.</i> , <b>60B</b> , 786 (1927).
Hydrogenation of maleic acid in aqueous solution; hydrogenation of cyclohexene in an alcoholic solution at 15 to 20° and under atmospheric pressure.	Metallic Re.	Ceramic material weak catalyst, but active for the dehydrogenation of alcohol.	Platonow, Anissimow and Krascheninnikowa: <i>Ber.</i> , <b>68</b> , 761-765, May 8, 1935.
Hydrogenation of cinnamic acid and its methyl, ethyl, propyl and <i>n</i> -butyl, benzyl and phenyl esters.	Ni (pure Ni and Ni on silicic acid decrease greatly the hydrogenation velocity).	Kieselguhr.	Kailan and Hardt: <i>Monatsh., Chem.</i> , <b>58</b> , 307-368 (1931).
Hydrogenation of benzene to cyclohexane.	30% Pt.	Asbestos.	
Hydrogenation of commercial phenols in the vapor phase.	Ni formate; 10-15% Ni nitrate (impregnated).	Chamotte.	Snelling: U.S.P. 122,811.
Hydrogenation of crotonic aldehyde to butyl aldehyde.	Cu.	Liquid glass.	Badische Anilin u. Soda Fabrik: G.P. 362,537 (1921).

Table 6 (Continued).

Reaction	Catalyst	Carrier	Observer
Hydrogenation of pyridine.	10% Pd.	Asbestos.	Zelinsky and Borisoff: <i>Ber.</i> , 57, 150-153 (1924).
Hydrogenation of primary aromatic amines at 175-250°; hydrogenation of aniline at 175° and under 150-240 atm. for 5 to 8 hours.	Soluble Ni (impregnated; treated with a basic carbonate; NiCO <sub>3</sub> ppt. under high pressure reduced).	Kieselguhr.	Goodyear Tire and Rubber Co.: F.P. 750,903, August 22, 1933.
Hydrogenation of substituted nitrostyrols.	Pd.	Bone charcoal.	Reichert and Koch: <i>Ber.</i> , 68, 265-274 (1935).
Hydrogenation of aromatic hydrocarbons.	A non-base exchangeable component acting catalytically.	Permutogenetic body.	Selden Co. (Jaeger): E.P. 306,803, April 24, 1929; Can. P. 296,913, January 21, 1930.
Hydrogenation of aromatic hydrocarbons under high pressure.	Ni.	Kieselguhr.	Shorel, Tulleners and Waterman: <i>J. Inst. Pet. Tech.</i> , 18, 179-182 (1932).
Hydrogenation of furan nucleus; almost quantitative yield of pure tetrahydrosylvan.	Os.	Asbestos.	Zelinsky and Schuikin: <i>Compt. rend. Acad. Sci. (U.R.S.S.)</i> , 60-65 (1933).
Pressure hydrogenation of naphthalene and benzene.	NH <sub>3</sub> molybdate sol and H <sub>2</sub> S or NH <sub>3</sub> vanadate.	Active charcoal.	International Hydrogenation Patents Co. Ltd.: F.P. 728,287, July 4, 1932; E.P. 379,587, September 22, 1932.
Hydrogenation of naphthalene at 325° under 100 atm. hydrogen pressure for 3 hours; conversion into tetrahydronaphthalene with a theoretical yield.	20% NiO.	Silica gel or kaolin (clarite); used twice on kaolin; 3 times on kieselguhr; 4 times on ppt. and glowed SiO <sub>2</sub> ; 6 times on magnesite; 7 times on florida earth; 8 times on tonsil; 27 times on silica gel.	Brochet and Schmitz: U.S.P. 1,896,282, February 7, 1933.
Mutual hydrogenation of cresols and naphthalene.	NH <sub>3</sub> molybdate.	Charcoal.	Kljukwin, Polozow and Lobuss: <i>Chimja tverdogo Topliva</i> , 5, 357-372 (1934).
Hydrogenation of castor oil and oleic acid.	Pd.	Finely divided Ni or Mg (Pb, Al, Fe, or Zn have autocatalytic action).	Ellis: "Hydrogenation of Organic Substances," N. Y., D. Van Nostrand Co., 1930; refer to Karl's Inaug. Dissert. Erlangen (1911).
Hydrogenation of oils (camphor oils).	Metal layers.	Silica gel.	Morris and Reyerson: <i>J. phys. Chem.</i> , 31, 1332-1337 (1926).
Hydrogenation of fatty oils.	Ni.	Active charcoal, kieselguhr or pumice.	Uno and Saida: <i>J. Soc. Chem. Ind. Japan</i> , 30, 107B (1927).
Hydrogenation of oils.	Ni.	Kieselguhr, charcoal, or pumice.	Jozsa: <i>Z. angew. Chem.</i> , 41, 767-771 (1927).
Hydrogenation of oils at a temperature higher than 300°.	Alkali metals.	Wood charcoal, coke powder.	Erdöl u. Kohle Verwertung A.-G.: G.P. 469,228 Kl 12a Gr 1 December 13, 1928.
Hydrogenation of oils.	Ammonium nickel oxide or hydroxide (impregnated).	Acid white clay.	Tonaka, Miroshita, Maeda and Heno: Japanese P. 100,179, March 20, 1933.

Table 6 (Continued).

Reaction	Catalyst	Carrier	Observer
Conjugated hydrogenation of soya bean oil with ethyl alcohol at 250°.	Ni.	Kieselguhr.	Pastuscheni: <i>Masloboino Zhivoe Delo</i> , 9, (No. 1), 21-22 (1933).
Hydrogenation of fats; 2-3 atm. H <sub>2</sub> and temperature above the solidification point of the saturated fat.	Pd; 1 p. Pd suffices to convert in a few hours 100,000 p. of oily material into a firm mass.	Carriers.	Verein Chemische Werke (Paal): G.P. 236,488 (1910); Brit. P. 18,642, August 6, 1911. Schlink & Co. A.-G. (Paal): G.P. 252,320 (1911); Brit. P. 5,188 (1911).
Hydrogenation of fats.	Ni.	Kieselguhr.	Kaiser: U.S.P. 1,004,034 (1911); U.S.P. 1,008,474 (1911).
Hydrogenation of fats.	Ni.	Wood charcoal.	Ellis: U.S.P. 1,060,673 (1912). Dewar: Brit. P. 15,668 (1914).
Solidification of fats.	Cu, Ni, Fe, Co, Pt melted together.	Chamotte.	
Solidification of fats.	Pd.	MgO.	Paal and Karl: <i>Ber.</i> , 46, 3069 (1913).
Solidification of oils.	Pd.	Inert substance.	Vereinigte Chemische Werke A.-G.: G.P. 236,488, August 6, 1910; Brit. P. 18,642 (1911).
Solidification of oils.	No base exchangeable component used as a catalyst.	Permutogenetic body.	
Oil hardening.	Pd.	Kieselguhr.	Vereinigte Chemische Werke A.-G. (Paal): G.P. 236,488, July 7, 1911.
Hydrogenation of hydrocarbons: tars, mineral oils, benzene, naphthalene, anthracene.	Ni hydrate paste with nitrates of Ag, V, Co, Cd or their alloys incorporated.	Metal spirals, metal wire, net rolls; the carrier metals are coated with the paste, heated to 240-280° for 40-60 hrs., before application and reduced with dry hydrogen.	Société Ind. des Carburant et Solvant: F.P. 792,507, January 4, 1936.
Hydrogenation of coal at 50 atm. pressure.	Ag, Au, Ru, Rh, Os, Pd, Ir, or Pt, or their compounds.	Magnesia or magnesite.	I. G. Farbenindustrie A.-G.: E.P. 275,670, October 5, 1927; E.P. 295,587, October 10, 1928.
Pressure hydrogenation of fuels.	Colloidal Re or its compounds in a colloidal state, e.g., Re sulfide (ppt. with H <sub>2</sub> S, acidified with H <sub>2</sub> SO <sub>4</sub> —sol of R.ReO <sub>4</sub> ).	Active charcoal.	N. V. deBataafsche Petroleum Maatschappij: E.P. 358,180, October 29, 1931.
Pressure hydrogenation of baked coal.	Al molybdate solution (impregnated).	Charcoal.	I. G. Farbenindustrie A.-G.: F.P. 736,863, November 30, 1932.
Pressure hydrogenation of coal or oil suspensions of coal.	Co, Ni, Cu, Ce <sub>2</sub> O <sub>3</sub> and Cr <sub>2</sub> O <sub>3</sub> .	Monazite and sand.	Shering and Kahlbaum A.-G.: F.P. 739,770, July 7, 1932.

Table 6 (Continued).

Reaction	Catalyst	Carrier	Observer
Hydrogenation of fuels (intermittent pressure).	Active iron ppt.	Infusorial earth.	I. G. Farbenindustrie, A.-G.: E.P. 381,367, October 27, 1932.
Pressure hydrogenation of fuels: coal, pitch.	MgCl <sub>2</sub> , NaHSO <sub>4</sub> or NaOH together with Zn or Al dust.	Bauxite, infusorial earth, aluminum hydrosilicate.	Kern: U.S.P. 1,852,709, April 5, 1932.
High pressure and temperature hydrogenation of coal at 460° for 3 hours; 93% of coal converted into liquid hydrocarbons.	NH <sub>3</sub> molybdate solution (0.1% of MoO <sub>3</sub> ).	Charcoal.	I. G. Farbenindustrie A.-G.: G.P. 570,951, Cl 120, February 22, 1933; F.P. 738,995, January 4, 1933.
Hydrogenation of fuels.	Finely dispersed colloidal MoS <sub>2</sub> .	Active charcoal (the greater part of which has been freed from ash by an acid treatment).	N. V. deBataafsche Petroleum Maatschappij: F.P. 745,074, May 2, 1933.
Pressure hydrogenation of fuels at 425° and under 200 atm. pressure.	Halide compounds of Mo, U, V, or iodine compounds of Ag, Cu, Ti, Sn, Mn, Ni and Co or their mixtures.	Active charcoal, silicic acid gel or pumice.	I. G. Farbenindustrie A.-G.: F.P. 747,459, June 17, 1933.
Hydrogenation of solid carbon-containing substances such as brown coal and bituminous coal by impregnating them with the catalyst in an organic solvent.	Molybdic acid in CH <sub>3</sub> OH (the coal contains 0.02% of molybdic acid).	Bituminous coal; the reacting substance itself serves as a carrier for the catalyst.	International Hydrogenation Patents Co. Ltd. I. G. Farbenindustrie A.-G.: E.P. 427,275, May 16, 1935; F.P. 778,674, March 22, 1935.
Pressure hydrogenation of carbonaceous materials (coal or high-boiling oil fractions).	Pd or its cmpds.: oxides, sulfides, chromates, halogenates, acetates, the catalyst may contain also such metals as Sn, Ge, Mo, Cr, W, Re, V, Fe, Al or their oxides, halides, sulfides or sulfur.	Charcoal.	International Hydrogenation Patents Co. Ltd. F.P. 793,799, January 31, 1936.
Pressure hydrogenation of solid carbon-containing substances such as brown coal, pitch, "torbanit," wood, especially bituminous coal at 380-470° under 200 to 300 atmospheres' hydrogen pressure.	Sn oxalate or Mo acid.	Reacting substances themselves are carriers.	Imperial Chemical Industries, Ltd.: F.P. 775,721, January 8, 1935; E.P. 425,679, April 18, 1935.
Hydrogenation of solid carbon-containing substances at 400° under 100 atmospheres hydrogen pressure.	Na aluminate.	Coal powder formed into paste with anthracene oil (c.p. over 250°).	Co. des Mines de Vicoigne (Noeu and Drocourt): E.P. 447,930, June 25, 1936.
Destructive hydrogenation of mineral or tar oils under pressure.		Coal paste.	Zotos: E.P. 386,993, February 23, 1932.
Hydrogenation and cracking of oils.	Iron oxide.	Cement together with catalyst formed into sticks with a wooden stick or sawdust in the middle.	Gyro Process Corporation (Harnsberger and Smith): U.S.P. 1,873,707 and 1,874,943 (1932).
Destructive hydrogenation of fuels.	MoS <sub>2</sub> obtained in fine dispersion when NH <sub>3</sub> molybdate is precipitated with H <sub>2</sub> S and the ppt. treated with H <sub>2</sub> (300 atmospheres).	Active charcoal.	N. V. deBataafsche Petroleum Maatschappij F.P. 745,468, May 11, 1933.



Table 6 (Continued).

Reaction	Catalyst	Carrier	Observer
Cracking and hydrogenation of oils.	Hydrides of As, Sb, Bi, B and Sn or Si or halide cmpds. such as $\text{BBr}_3$ (precipitated in the absence of O <sub>2</sub> ); for pressure hydrogenation.	Metal oxides such as $\text{CaO}$ , $\text{BaO}$ , active charcoal, asbestos, graphite, $\text{ZnO}$ or $\text{MgO}$ .	I. G. Farbenindustrie A.-G. (Mittasch and Zorn); U.S.P. 1,895,764, January 31, 1933.
Destructive hydrogenation of solid carbon-containing substances such as bituminous coal at 410–480°.	0.2% $\text{PbCl}_2$ formed into a paste with oil (1 : 1); the halides of P, S, Se, As and Sb may be used.	Bituminous coal, itself serves as a carrier.	International Hydrogenation Patents Co. Ltd. F.P. 793,464, January 25, 1936.
Destructive hydrogenation of tars; sp. wt. of the hydrogenated product 0.004 per 10 kg. tar (low-temperature tar) and 0.0007 per 10 kg. tar for 1 kg. catalyst, respectively.	Impregnated with $(\text{NH}_4)_2\text{MoO}_4 \cdot 4\text{H}_2\text{O}$ , after drying, the catalyst contains 25% of ammonium molybdate, activation by preliminary heating in air at 500°, $\text{Mo}_2\text{O}_4$ formed.	Glowed, grainy Al gel.	King and Cawley: <i>Dept. Sci. Ind. Res. Fuel, Res. Tech. Paper No. 41</i> , 17 p. (1936).
Determination of gaseous olefins or hydrogen through catalytic hydrogenation.	Melted Ni nitrate.	Asbestos (purified by $\text{HNO}_3$ ).	McMillan, Cole and Ritchie: <i>Ind. Eng. Chem. (Anal. Ed.)</i> , <b>8</b> , 105–107, March 15, 1936.

Table 7. Carriers in Dehydrogenation Reactions.

Reaction	Catalyst	Carrier	Observer
$\text{C}_2\text{H}_2 + \text{NH}_3 \rightarrow \text{CH}_3\text{CN} + \text{H}_2$	$\text{ThO}_2$ , $\text{ZrO}_2$ .	Mud ore, bauxite, Permutite.	Rhenania Verein Chem. Fabrik: G.P. 367,538 (1918). I. G. Farbenindustrie A.-G.: G.P. 477,049 (1927).
Catalytic dehydrogenation.	$\text{ZnS}$ or $\text{CdS}$ .	Pumice.	I. G. Farbenindustrie A.-G.: E.P. 262,120, January 26, 1927.
Dehydrogenation of lower aliphatic alcohols in the gaseous state to ether and $\text{C}_2\text{H}_4$ at 135°; $\text{CH}_3\text{OH}$ to $\text{CH}_3\text{OCH}_3$ at higher temperatures.	Sirupy $\text{H}_3\text{PO}_4$ (dehydrogenates to a high extent) conc. $\text{H}_2\text{SO}_4$ .	Pumice.	Senderens: <i>Compt. rend Acad. Sci.</i> , <b>192</b> , 1335–1337, June 1, 1931.
Dehydrogenation process.	Conc. solution of mixtures of metallic salts, e.g., Cu, Cr, or Mg which split off their volatile acids at higher temperature without leaving the catalyst poisons.	Pumice or coke.	Howards and Sons, Ltd.: (Blagden and Clark): E.P. 363,776, January 21, 1932.
Dehydrogenation of organic compounds.	Halogen cmpds. of Cu, Ag, Zn, Cd, Pb, Sn, Ti, Si, V, Bi, Mo, W, U, Mn, Re, Ni, Fe, or Co.	Active charcoal or active $\text{SiO}_2$ .	I. G. Farbenindustrie A.-G.: F.P. 748,442, July 4, 1933.
Dehydrogenation of aromatic hydrocarbons at 500–800°.	Difficultly reducible but fusible metal oxides or compounds decomposed into oxides (a mixture of potash, $\text{ThO}_2$ and $\text{CoO}$ ).	Pumice.	I. G. Farbenindustrie A.-G.: Brit. P. 369,613, December 17, 1930.
Preparation of aromatic hydrocarbons unsaturated in the side chain from the corresponding saturated aromatic hydrocarbon under strongly diminished pressure.	Dehydrogenation catalyst; mixed basic Cu, Fe, Ni.	Pumice.	Snida: Austrian P. 132,642, February 25, 1933.

Table 7 (Continued).

Reaction	Catalyst	Carrier	Observer
Dehydrogenation of cyclohexane.	Ni. Pd.	Al <sub>2</sub> O <sub>3</sub> . Asbestos.	Balandin: <i>Z. phys. Chem.</i> (B), 19, 451-461 (1932).
Dehydrogenation of methyl cyclohexane to toluene at 290-300°.	Pt.	Active charcoal (30 g. active charcoal stirred with H <sub>2</sub> PtCl <sub>6</sub> solution containing 5.2 g. Pt).	Packendorff and Leder-Packendorff: <i>Ber.</i> , 67, 1388-1391, August 8, 1934. Zelinsky and Borissov: (Refer to C. 1924 I 1142).
Dehydrogenation of pyrroline to a mixture of pyrrol and pyrrolidine.	Pt (8 cm. layer).	Asbestos.	Wibaut and Proost: <i>Rec. trav. Chim.</i> , 52, 333-336 (1933).
Dehydrogenation of isoborneol (preparation of camphor).	Base non-ferrous metal catalysts (Cu, Zn, Mn, Cd, Sn, Pb, Ag); salts of metals (Cu(NO <sub>3</sub> ) <sub>2</sub> , Zn(NO <sub>3</sub> ) <sub>2</sub> ) capable of forming soluble complex ions with nitrogen bases, such as NH <sub>4</sub> OH; when NH <sub>4</sub> OH is added in excess to a solution of one or more of these salts, a clear solution is obtained; on heating this solution and slowly discharging the NH <sub>3</sub> , a precipitate of a granular character is formed consisting of the metal hydroxide.	Kieselguhr.	E. I. Du Pont de Nemours & Co.: E.P. 392,134, June 1, 1933.
Dehydrogenation of mineral oils and naphthenes at 200-300° at elevated or diminished pressure.	NH <sub>4</sub> molybdate, Pb(NO <sub>3</sub> ) <sub>2</sub> , and H <sub>3</sub> PO <sub>4</sub> treated with H <sub>2</sub> S at 300°;	Active charcoal.	I. G. Farbenindustrie A.-G.: E.P. 333,995, September 18, 1930.
	NH <sub>4</sub> tungstate, Co(NO <sub>3</sub> ) <sub>2</sub> , and Sb <sub>2</sub> O <sub>3</sub> treated with H <sub>2</sub> S at 350°;	Active charcoal.	
	NH <sub>4</sub> vanadate, Co(NO <sub>3</sub> ) <sub>2</sub> , and H <sub>3</sub> PO <sub>4</sub> treated with H <sub>2</sub> and CS <sub>2</sub> at 350°; mixture brought on the carrier.		
Dehydrogenation of 43%-crude oil with a high per cent of aromatic hydrocarbons at 160°.	30% Pt Ni	Active charcoal. Al <sub>2</sub> O <sub>3</sub> .	Zelinsky and Schuikin: <i>Zhur. Obshchei Khim.</i> , 4, (66) 901-905 (1934).
Dehydrogenation of pressure hydrogenation products.	Dehydrogenation catalysts or compounds of the 6th group, e.g., Mo oxides or ZnO. Al <sub>2</sub> O <sub>3</sub> ; likewise mixed with CdS, ZnS, or Cr <sub>2</sub> O <sub>3</sub> .	Active charcoal.	I. G. Farbenindustrie A.-G. (Mittasch, Pier, Wietzel and Langheinrich): U.S.P. 1,913,940 and 1,913,941, June 13, 1933.
Dehydrogenation of benzene, hydrogenation products of coal, or hydroaromatics such as cyclohexane at 430°.	FeCl <sub>3</sub> , Al(OH) <sub>3</sub> and Cr(OH) <sub>3</sub> .	Charcoal. Silicic acid gel.	I. G. Farbenindustrie A.-G.: F.P. 448,442.
Dehydrogenation of a fraction of Surachan benzene (Baku), rich in hydroaromatics.	Ni. Pt.	Al <sub>2</sub> O <sub>3</sub> . Active charcoal.	Zelinsky and Schuikin: <i>Izvestiya Acad. Nauk. (S.S.S.R.)</i> , 7, 229-237 (1935).
Preparation of dehydrogenation catalysts by activating non-glazed alumina with a small amount of heavy metal oxides.	Metal oxides of the 6th to 8th groups of the periodic system; such as CuSO <sub>4</sub> , Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , MnO or CoO.	Glazed alumina.	I. G. Farbenindustrie A.-G.: F.P. 679,998, April 23, 1930.

Table 8. Carriers in Polymerization and Condensation Reactions.

Reaction	Catalyst	Carrier	Observer
Polymerization of gaseous hydrocarbons $C_2H_4$ and $C_3H_6$ into liquid at 260-540° temperature and under 40 to 120 atms. pressure.	$AlCl_3$ , $AlBr_3$ ; metal halides; Pd-Pt sponge; finely dispersed alloys; metals of the 8th group.	Silica gel, active charcoal, fuller's earth.	Pure Oil Co.: F.P. 680,038, April 24, 1930.
Polymerization of propylene at 350°.	$Al_2O_3$ (adsorbed on $SiO_2$ ).	Porous $SiO_2$ .	Gayer: <i>Ind. Eng. Chem.</i> , <b>25</b> , 1122-1127 (1933).
Polymerization of propylene under 10 kg./cm <sup>2</sup> .	$H_3PO_4$ and $P_2O_5$ (1:1).	Diatomaceous earth; silica gel; activated charcoal; petroleum coke.	Ipatieff and Schaad: (unpublished) U.O.P. Ipatieff: <i>Ind. Eng. Chem.</i> , <b>27</b> , 1067 (1935).
Polymerization of butylenes.	30% solid phosphoric acid.	Diatomaceous earth.	Ipatieff and Schaad: (unpublished) U.O.P.
Polymerization of isobutene.	$Al_2O_3$ .	Silica gel.	Waterman, Leenderste and de Kok: <i>Rec. trav. Chim. Pays-Bas</i> , <b>53</b> , (4) 15, 1151-1158, December 15, 1934.
Condensation with dehydration; preparation of diethyl aniline from aniline and alcohol at 370-375°.	$ThO_2$ .	Asbestos.	Chandra: <i>J. Ind. Chem. Soc.</i> , <b>5</b> , 383 (1928).
Condensation of acetylene with primary amines.	$ZnBr_2$ .	Pumice.	G.P. 516,765 (1930).
Condensation of acetylene with acetic acid.	Mercuric sulfate prepared from $HgO$ in acetic acid by means of $H_2SO_4$ with 50% $SO_2$ .	Japanese acid ton (not only accelerates the reaction, but triples the yield).	Kuwata and Kato: <i>J. Soc. Chem. Ind. (Japan) Sup.</i> , <b>39</b> , 127B-128B (1936).

Table 9. Carriers in Hydration Reactions.

Reaction	Catalyst	Carrier	Observer
Hydration of ethylene hydrocarbons at 150°, yield, 15-20% alcohol.	$CuO \cdot WO_3$ .	Active charcoal.	N. V. de Bataafsche Petroleum Maatschappij: Brit. P. 335,551.
Hydration of ethyl ether; 40% converted into acetone, 10% into ethyl alcohol and 18% into ethylene.	12 g. hydroxide prepared from 100 g. $Al$ -100 g. finely dispersed iron oxide (filtered dried at 120-130°).	$MgO$ .	Kagan, Kossinskaja and Tschernizow: <i>Zh. obsht. Chimii</i> , <b>3</b> , (65) 337-344 (1933).
Hydration of ethylene in the preparation of ethyl alcohol at 150°; 2% yield.	70% $H_2SO_4$ - $Ag_2SO_4$ (fatigue of the catalyst is a disadvantage).	Active charcoal.	Balandin and Neswishsky: <i>Sc. Communic. Moscow Univ.</i> , <b>2</b> , 233-235 (1934).

Table 10. Carriers in Dehydration Reactions.

Reaction	Catalyst	Carrier	Observer
Dehydration of alcohols.	Pt.	Asbestos.	I. G. Farbenindustrie A.-G.: E.P. 357,749, October 22, 1931.
Dehydration of formic acid at 280-330°.	$TiO_2$ - $Al$ phosphate (activity only temporary). $P_2O_5$ .	Silica gel.	Graeber and Cryder: <i>Ind. Eng. Chem.</i> , <b>27</b> , 828-831 (1935).
Dehydration of $CH_3COOH$ to acetic anhydride at 400-450°.	$H_3PO_4$ (impregnated).	Silicon carbide.	Dreyfus: Brit. P. 312,733. British Celanese Co.: Brit. P. 312,587.
Dehydration of alcohols.	Ni, Cu, or Ag, $CuO$ , $CuO \cdot Ag_2O$ , $Cr_2O_3$ , $MnO$ , $ZnS$ ; also selenides and phosphides.	Glassy clay.	I. G. Farbenindustrie A.-G.: E.P. 313,426, July 11, 1929.

Table 10 (Continued)

Reaction	Catalyst	Carrier	Observer
Dehydration of alcohols.	CuSO <sub>4</sub> (impregnated).	Al <sub>2</sub> O <sub>3</sub> .	I. G. Farbenindustrie A.-G.: F.P. 679,998.
Dehydration of isoamyl alcohol.	NaPO <sub>3</sub> .	Bauxite.	I. G. Farbenindustrie A.-G.: E.P. 367,892, March 24, 1932.
Dehydration of alcohols to olefins.	CuO, CuO+Ag <sub>2</sub> O, Cr <sub>2</sub> O <sub>3</sub> , NiO, H <sub>3</sub> PO <sub>4</sub> or acid salts Na <sub>2</sub> HPO <sub>4</sub> , Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> .	Alumina (activated at 427°).	Ipatieff: (1902) Brit. P. 13,426 and 326,185 (1934). Ipatieff and Corson: <i>Ind. Eng. Chem.</i> , 27, 1069 (1935).
Dehydration of ethyl alcohol.	Al <sub>2</sub> O <sub>3</sub> .	Birchwood charcoal.	Adadurow and Kraini: <i>Zhur. Fiz. Khim.</i> , 15, 136-144 (1934).
Dehydration of butyl alcohol at 250° and 350-400°.	90% H <sub>3</sub> PO <sub>4</sub> ; Br added.	(a) Al <sub>2</sub> O <sub>3</sub> . (b) Pumice stone.	Komarewsky, Johnstone and Joder: <i>J. Am. Chem. Soc.</i> , 56, 2705 (1934). Faworski: (1890).
Dehydration of ethyl alcohol.	H <sub>2</sub> SO <sub>4</sub> .	Glowed kaolin.	Deymann: (1795); refer to <i>Bull. Soc. Chim.</i> , 2, 1000 (1935).
Dehydration of alcohol.	HNO <sub>3</sub> (33%) in amount of 62.5%.	Glowed kaolin (water content 1%).	Larin and Tscherepnjew: Russ. P. 41,504, February 28, 1935.
Joint dehydration of ammonia, methyl, ethyl, n-propyl and n-butyl alcohols.	Blue tungsten oxide, alumina, NiO, CeO, ThO <sub>2</sub> .	Silica gel, pumice; silica gel prepared at 465° most active.	Brown and Reid: <i>J. Phys. Chem.</i> , 28, 1067 (1924).
Dehydration of ammonia plus ethyl alcohol.	Th, blue tungsten oxide.	Alumina, silica gel, kaolin.	Briner and Gemdillon: <i>Helv. Chim. Acta</i> , 14, 1283 (1931).
Dehydration of o-hexahydrocresol.	CuO.	Alumina.	Ipatieff and Rutala: <i>J. Russ. phys.-Chem. Soc.</i> , 44, 1692 (1912).
Dehydration of phenols.	Th (heated electrically in the tube); temperature, 350-525°.	Glazed porcelain tube.	Briner and Bron: <i>Helv. Chim. Acta</i> , 15, 1234-1241 (1932).
Preparation of p-cymol from tertiary alcohols at 160-220°.	Dehydrating catalyst is the carrier itself.	Fuller's earth or kieselguhr; active charcoal Al <sub>2</sub> O <sub>3</sub> .	Bennett and Frazer: U.S.P. 1,893,879, January 10, 1933.

Table 11. Carriers in Desulfurization Processes.

Reaction	Catalyst	Carrier	Observer
Desulfurization of carbon-containing substances, such as petroleum asphalt.	MoO <sub>3</sub> , precipitated.	Active charcoal.	N. V. deBataafsche Petroleum Maatschappij: Jugoslav P. 9,950, May 1, 1931.
Desulfurization of a crude-oil fraction at 440-480° temperature and under 85 to 100 atm. H <sub>2</sub> pressure.	MoO <sub>3</sub> (NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> , colloidal Mo- and Cu chromite.	Active charcoal.	Pertierra: <i>Anal. soc. espan. fis. quim.</i> , 31, 289-310, July 15, 1933.
Desulfurization of hydrocarbon oils.	CuO, CuCl <sub>2</sub> , HgCl <sub>2</sub> , FeCl <sub>3</sub> .	Fuller's earth, dry ton; ex: (1) 90% dry ton 5% KMnO <sub>4</sub> 5% CuCl <sub>2</sub> (2) 95% dry ton 5% CuCl <sub>2</sub> (3) 1-8% HgCl <sub>2</sub> (CoCl <sub>2</sub> , CdCl <sub>2</sub> ) 1-30% CuCl <sub>2</sub> Bal. dry ton	Bennett-Clark Co. (Hoover): U.S.P. 2,042,050, August 10, 1935; U.S.P. 2,042,051 to 2,042,054, May 26, 1936.

Table 12. Carriers in Chlorination Reactions.

Reaction	Catalyst	Carrier	Observer
$\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$ $\text{C}_2\text{H}_2 + 2\text{Cl}_2 \rightarrow \text{C}_2\text{H}_2\text{Cl}_4$	$\text{SbCl}_5$	Active charcoal.	Askenasy and Mugdan: G.P. 154,657 (1903).
Chlorination of $\text{C}_2\text{H}_2$ by $\text{HCl}$ .	$\text{ZnCl}_2$	Silica gel.	Wibaut and van Dalfsen: <i>Rec. trav. Chim. Pays-Bas</i> , 51 (4) 13, 636-640, June 15, 1932.
$\text{CH}_2 : \text{CH}_2 + \text{HCl} \rightarrow \text{C}_2\text{H}_4\text{Cl}$	$\text{BiCl}_3$	Asbestos.	Wibaut: G.P. 445,981 (1928).
Preparation of dichloroethylene. $\text{ClCH} : \text{CHCl}$ , by leading $\text{C}_2\text{H}_2$ with $\text{Cl}_2\text{CCH}_2\text{Cl}$ or $\text{Cl}_2\text{HCCHCl}_2$ at $350^\circ$ .	Ni.	Active charcoal.	Chemische Fabrik Heyden A.-G. (Wiegand): G.P. 566,034, April 2, 1931.
Chlorination of amylenes and ethylene.	80% $\text{H}_3\text{PO}_4$	Diatomaceous earth.	Ipatieff and Schaad: U.O.P.
Chlorination of propylene.	$\text{Fe}_2\text{O}_3$	Porous and adsorbing $\text{Al}_2\text{O}_3$ , florida earth, $\text{SiO}_2$ .	Gayer: <i>Ind. Eng. Chem.</i> , 25, 1122-1127 (1933).
Chlorination of methane with $\text{Cl}_2$ or $\text{HCl}$ at $450^\circ$ ; 89% yield $\text{CH}_3\text{Cl}$ with $\text{CH}_4$ ten times in excess.	$\text{CuCl}_2 + 1\% \text{ CeCl}_3$ (4 hrs. treatment with $\text{N}_2$ at $150^\circ$ ).	Pumice.	Giordani: <i>Ann. Chim. Applicata</i> , 25, 163-173 (1935).
Preparation of tertiary alkyl monochlorides from gaseous or liquid olefins.	20% $\text{SnCl}_4$ (impregnated at $150^\circ$ ).	Active charcoal.	Prins: <i>Rec. trav. Chim. Pays-Bas</i> , 51, 1065-1080 (1932).
Preparation of alkyl chlorides at $220^\circ$ .	Less than 50% $\text{H}_3\text{PO}_4$ .	Carrier.	Walker Gesellschaft f. Elektr. Industrie G.m.b.H. (Ernst): G.P. 583,497, Kl 12o, September 4, 1933; add to G.P. 541,566.
Ethyl halogenides prepared from $\text{C}_2\text{H}_4$ and hydrogen halide.	$\text{ZnCl}_2$ in an active form; activators: halides of Li, Mg, Ca, Cu, Sn.	Wood charcoal or active $\text{SiO}_2$ .	I. G. Farbenindustrie A.-G.: F.P. 793,744, January 30, 1936.

Table 13. Carriers in Miscellaneous Reactions.

Reaction	Catalyst	Carrier	Observer
Preparation of $\text{H}_2$ from hydrocarbons in the presence of water vapor, $\text{CO}_2$ , or $\text{O}_2$ .	Fe, Ni, Co in a mixture with Al compounds containing $\text{O}_2$ and one or more elements: Si, $\text{H}_2$ , C, B, P.	Al silicate, bauxite, kaolin.	I. G. Farbenindustrie A.-G.: E.P. 323,855, February 6, 1930.
Preparation of hydrogen from hydrocarbons passed with water vapor, oxygen, or $\text{CO}_2$ .	Mixture of Fe, Ni or Co.	Kaolin or bauxite.	I. G. Farbenindustrie A.-G.: Brit. P. 323,855, F.P. 677,826 (1930).
Hydrogen prepared from hydrocarbons, saturated or unsaturated, higher than $\text{CH}_4$ , with temperature below $1000^\circ$ by water vapor or $\text{CO}_2$ .	Fe, Co, Ni.	Hydraulic binding materials.	I. G. Farbenindustrie A.-G.: F.P. 729,119, July 19, 1932.
Conversion of hydrocarbons and water vapor in the preparation of $\text{H}_2$ .	Alloys with equal amounts of Ni and Cr; 20 and 24 percent.	Inert carriers.	Tröger: <i>Petroleum</i> , 28 (N. 34) 1-9, August 24, 1932.
Preparation of unsaturated hydrocarbons.	Metallic or oxidic catalysts, e.g., Ni, Co, Cu or Zn (substituted with an activator such as $\text{CaCO}_3$ ).	Pumice.	Dreyfus: F.P. 749,916, August 1, 1933.

Table 13 (Continued).

Reaction	Catalyst	Carrier	Observer
Conversion of gases or vapors.	Th oxide and ZnO finely dispersed.	Silica gel.	I. G. Farbenindustrie A.-G. (Kotzer and Stöweker): U.S.P. 1,828,380 (1930); G.P. 509,582, Cl 12g, October 10, 1930.
Preparation of higher ketones from aliphatic alcohols (acetone) at 150–400°.	15% Cu formate + 1.8% MoO <sub>3</sub> .	Active alumina (treated with a mixture of air and water vapor at 450°).	Deutsche Gold u. Silber Scheideanstalt (Roesler): F.P. 741,385, February 10, 1933.
Preparation of butene from butanols.	Activated alumina 30% H <sub>3</sub> PO <sub>4</sub> (89%) 80% H <sub>3</sub> PO <sub>4</sub> (89%) 50% H <sub>3</sub> PO <sub>4</sub>	Diatomaceous earth.	Ipatieff and Schaad: U.O.P.
Preparation of maleic acid anhydride, C <sub>4</sub> H <sub>2</sub> O <sub>3</sub> , at 475–550° and contact time 0.1–0.25 sec.	Metal oxides of the 3rd and 6th groups; V oxide activated with Al, Mg, Mn, Mo.	Difficultly meltable porous carrier, "Alundum."	National Aniline and Chemical Co., Inc. (Pannett): U.S.P. 1,895,522, January 31, 1933.
Preparation of oxyalkyl amines.	Ni.	Kieselguhr.	I. G. Farbenindustrie A.-G.: (Schlichting) G.P. 573,983, Kl 12g, April 8, 1933.
Preparation of aliphatic amines from alcohols and NH <sub>3</sub> .	WO <sub>3</sub> , TiO <sub>2</sub> .	Silica gel, Al <sub>2</sub> O <sub>3</sub> or Cr <sub>2</sub> O <sub>3</sub> gels in conc. of about 20%.	E. I. Du Pont de Nemours & Co.: E.P. 384,714, January 5, 1933.
Preparation of light hydrocarbons from petroleum oils at 200° with H <sub>2</sub> .	Ni.	Fuller's earth.	Gray Processes Corp. (Gray): U.S.P. 1,878,580, September 20, 1932.
Catalytic influence in self-ignition processes for benzene without contact at 690°; contact reduces ignition point to 160°.	50% Pd.	Asbestos.	Zerbe, Eckert and Jentzsch: <i>Angew. Chem.</i> , 46, 659–662, October 21, 1933.
Preparation of hydroaromatic oxides such as methene oxide from chlormenthol and H <sub>2</sub> O vapor.	Cu phosphate.	Pumice.	Shering-Kahlbaum (Schoeller, Schwenk, Borgwardt and Kichner): G.P. 574,837, Kl 12o, April 20, 1933.
Isomerization of butenes.	Solid H <sub>3</sub> PO <sub>4</sub> , 30% H <sub>3</sub> PO <sub>4</sub> (89%).	Diatomaceous earth.	Ipatieff and Schaad: U.O.P.
Hydrolysis of organic halides.	Cu.	Highly porous silica.	Jenkins and Norris: U.S.P. 1,884,710, October 25, 1932.
Catalytic reaction.	Reducible Ni salts. Mixture reduced at 240–245° with H <sub>2</sub> .	Talc.	American Cotton Seed Oil Co. (Cluff): U.S.P. 1,381,969, June 21, 1921.

The list of carriers includes gels of a sponge-like structure; porous substances, such as inorganic masses, unglazed porcelain, pumice, bauxite, chamotte, kaolin, clay, various forms of carbon (bone charcoal, wood charcoal, etc.); fibrous materials, such as cellulose, cotton, asbestos, etc.; hydraulic binding materials, such as compounds formed with calcium hydroxide and having properties of hydraulic cements, the simplest being gypsum, CaSO<sub>4</sub>·2H<sub>2</sub>O, Portland cement clinkers, etc.; earths (natural silica abrasives), which are light, loose, powdery materials, less firmly coherent, with a fine, uniform grain, such as diatomaceous earth (diatoms are any microscopic unicellular marine or fresh-water algae), infusorial

earth, japanese acid earth, tripolite, kieselguhr, etc.; compact surfaces, such as iron pellets, metals (platinum, palladium, copper), wires, nets, alloys of metals, granulated aluminum; salts, such as calcium carbonate, barium sulfate, or simple, as well as complex silicates; natural and artificial zeolites; materials in a colloidal state, such as gum, gelatin, dextrin, etc., or clay-like substances, such as Bentonite.

A knowledge of the nature and properties of carriers is a necessary guide in their selection as supports for catalysts. In addition to their structural characteristics (amorphous or crystalline, porous or compact surfaces), the following properties of carriers used in catalysis must be differentiated:

- (1) Chemical composition and state of dispersion.
- (2) Physical properties of the surface (porosity, adsorption, contact property, electrical properties, mechanical strength, etc.).
- (3) Amount and concentration of both catalyst and carrier; thickness of the catalyst layer deposited on the carrier; saturation capacity of carriers.
- (4) Active area of the carrier and the ratio of the catalyst atoms to the carrier atoms corresponding to the catalyzing action of the carrier-catalyst.

Carriers are quite often carbon-rich materials or substances containing a large proportion of silica and, less often, alumina compounds. Table 14 presents examples of carriers and their chemical composition.

Table 14. Chemical Composition of Carriers.

- |                            |                              |
|----------------------------|------------------------------|
| 1. Carbonaceous materials. | 5. Aluminates.               |
| 2. Simple silicates.       | 6. Various salts.            |
| 3. Complex silicates.      | 7. Minerals.                 |
| 4. Silicates of alumina.   | 8. Metals (Pt, W, Cu, etc.). |

#### Silicates

Silica gel ( $\text{SiO}_2$ ).

Natural silica abrasives: diatomaceous earth, infusorial earth, tripolite and kieselguhr.

Pumice: Silicates of Al, Na, K, Ca, Mg, Fe.

Asbestos: Chrysotile ( $\text{H}_3\text{Mg}_3\text{Si}_2\text{O}_{10}$ ).

Tremolite,  $\text{CaMg}_3(\text{SiO}_3)_4$ .

Actinolite,  $\text{Ca}(\text{MgFe})_3(\text{SiO}_3)_4$ .

Crocidolite (blue asbestos),

$\text{NaFe}(\text{SiO}_3)_2 \cdot \text{FeSiO}_3$ .

Composition varies:	$\text{SiO}_2$	40.36–58.80%.
	$\text{Al}_2\text{O}_3$	0.21–5.72%.
	FeO	0.66–37.00%.
	MgO	2.30–43.86%.
	CaO	0.5–10.65%.
	$\text{H}_2\text{O}$	0.5–13.45%.

Zeolites: Complex silicates.

Artificial zeolites: Ca aluminate silicates.

Na

Natural zeolites: (1) bases combined with alumina.

(2) bases " silica.

Clays: Hydrous silicates of alumina,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ —

39.53%  $\text{Al}_2\text{O}_3$ , 46.52%  $\text{SiO}_2$ , 13.95%  $\text{H}_2\text{O}$ .

Bentonite (clay-like material): 60.64%  $\text{SiO}_2$ , 23.26%  $\text{Al}_2\text{O}_3$ ,

3.92%  $\text{Fe}_2\text{O}_3$ , 0.59% CaO, 2.19% MgO, 4.33%  $\text{Na}_2\text{O}$ .

#### Aluminates

Alumina,  $\text{Al}_2\text{O}_3$ .

Corundum (natural aluminum oxide),  $\text{Al}_2\text{O}_3$ .

Bauxite: 55–65%  $\text{Al}_2\text{O}_3$ , 2–5% Silica, 1–25% ferric oxide,  
1–3% titanium oxide, 10–30% combined  $\text{H}_2\text{O}$ .

#### Cements

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (gypsum).

$\text{CaO} \cdot \text{Al}_2\text{O}_3$ .

$3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ .

Portland cement clinker: basic silicates and aluminates of lime.

Portland puzzolan cement: high silica cement

(active siliceous material—puzzolan).

### Dispersion and Physical Properties of the Carrier

The carrier may be either a coarse or a fine grain mass and it may be also in a colloidal state of dispersion. It is postulated that a carrier must be a substance catalytically inert with respect to the reacting components of the catalyzed system. In oxidation reactions, such as the formation of formaldehyde from methyl alcohol, it is recommended that an unoxidizable material (pumice, baked clay, or kieselguhr) be used as a carrier. Since alumina proves to be a catalyst in this reaction, Alundum is more suitable as a carrier in this case. When the catalyst is supported on a siliceous carrier, heating to a temperature at which silicates may be formed with the catalyst must be avoided. If a catalytic reaction requires such a temperature, magnesium oxide, alumina, natural bauxite, lime or calcium carbonate may be readily substituted for the above carrier. It is assumed that definite properties of a carrier, such as size of its pores or capillaries, adsorption ability, ability to exchange ingredients, resistance to mechanical stress and colloidal nature (plasticity, thixotropy, flocculation, coagulation, etc.) must be considered with regard to the distributing, depositing, or impregnating possibilities of a catalyst.

On the surface of each carrier are active forces of varying nature: (a) forces which attract molecules one to another and cause surface tension;<sup>48, 69</sup> (b) electrical forces, which distribute electricity between contacting layers of single phases in a definite manner and cause electro-capillary phenomena, contact electricity, etc., and (c) chemical forces, which act in contacting layers of two phases, causing a positive or a negative adsorption. Charcoal or silica gel, for example, are excellent adsorbents, their adsorption power depending chiefly on the degree of surface development, and the effect of their porosity is greater than the action of any other factor. In order to increase its activity, the charcoal surface, besides being porous, must contain certain groups of atoms, such as nitrogen or oxygen, so that it may be able to transfer the oxygen of the air to readily oxidizable substances.

The gels of silicic acid, even when heated in a vacuum up to 300° and dehydrated up to 3 per cent, possess a great-adsorption ability ranking with that of cocoanut charcoal. These gels may have up to 450 m<sup>2</sup> internal surface in one gram of substance. The amount of gas adsorbed increases with an increase in the surface of the adsorbent, with the concentration and pressure of the gas, as well as with a decrease in temperature. In comparison with other gases, those readily adsorbed have the highest boiling point. At first adsorption proceeds rapidly, and the first amounts of the adsorbate are retained more readily than the later ones. In solutions, adsorption by a solid proceeds in essentially the same way as that from a gaseous medium. Adsorption on charcoal and silica gel is a normal phenomenon in which the adsorption process is usually limited to a condensation of unchanged molecules; but, in many cases, adsorption does not follow the usual regularities because other forces come into play, the effects of orientation and selectivity gaining in importance.

Langmuir's investigations elaborate Bragg's work on the crystalline



structure of a substance in a solid state. Langmuir pictures the surface of a solid body as a checker-board consisting of strongly active and weakly active districts in which molecules or atoms of a gas may be condensed by combining them with certain atoms of the solid surface. Regarding the imperfect structure of the crystalline lattice, Langmuir conceived the notion of different degrees of saturation of the residual valences of both atoms and molecules, which are greater the more active the adsorbent. On the other hand, the adsorbent is not uniform, *i.e.*, smooth, but has sharp edges, dips, etc. It is a recognized fact that molecules or atoms which lie uppermost on the surface of the adsorbent have the greatest number of free bonds due to the absence of neighboring molecules or atoms, possess the greatest amount of energy, and have properties similar to those in the gaseous state. Taylor enlarged on the latter idea, ascribing to the separate units of the surface the ability to activate, and emphasized the significance of special active centers or points instead of active districts. According to Taylor's theory, isolated atoms (molecules) located in corners or on edges of crystals are less saturated with bonds than those found on the faces of crystals. Activation of the adsorbed molecules is caused by fields of forces originating in the unsaturated places of the crystalline lattice of the adsorbent.

The specific behavior of a catalyst supported by a carrier has been interpreted by applying adsorption conceptions.<sup>66</sup> It is postulated that if the resulting adsorption forces of a catalyst-carrier mass for saturated reacting compounds is greater than that for the unsaturated, it is suitable for dehydrogenation processes; otherwise the greater adsorption of unsaturated compounds will make it behave as a hydrogenating catalyst. In case a mixed adsorbent is used which has adsorption centers consisting of various molecules or aggregates, their fields of forces are determined by the combined action of both components.<sup>95</sup> If, for instance, active charcoal is mixed with silica gel, the latter will readily adsorb gases and vapors (ammonia, water vapor and organic substances), while the charcoal will more readily adsorb substances of an acid character, such as chlorine.

Other properties also change when two adsorbents are mixed. Gels precipitated with asbestos are very fragile and are readily converted into a powder. This effect is produced by adding 0.5 g. asbestos to the mass; with an increase in the amount of asbestos used, the gel becomes compact and difficult to break, because asbestos fibers become enmeshed, and act as a binding material. Gels precipitated in the presence of asbestos, as well as in the presence of pumice, are more active than in the absence of these substances. The ratio of the components involved is, of course, important, since the activity has been found to change periodically, resulting in maxima and minima action.

In using a carrier as a support for a catalyst, it is interesting to determine (1) the number of surface atoms present on the carrier and (2) the number of atoms of the catalyst precipitated on the carrier. From the number of pieces of charcoal and the volume occupied by them, it is possible to calculate the volume taken up by one piece of charcoal. From the average thickness of a piece of charcoal, its width and its length, both the

surface of one piece of charcoal and its total surface may be computed. Finally, knowing the distance between the carbon atoms, the actual surface occupied by one carbon atom may be obtained. The number of atoms in a given volume of the carrier is calculated by dividing the total surface of the charcoal by the surface occupied by one carbon atom. The number of atoms of catalyst precipitated on the carrier is obtained by dividing the number of atoms of the metal in one gram molecular weight multiplied by the weight of the metal (in a given volume of solution used for precipitating the weight of one gram molecule of the metal catalyst).

Quincke,<sup>84</sup> Mascart<sup>71</sup> and Vincent<sup>114</sup> determined the "radius of action" of a metal or a salt (covering materials) serving as carriers:

Table 14a.

(Quincke)

System	Limiting Thickness in $\mu\mu$
$\text{Ag}_2\text{S}-\text{Hg}$	49
Glass covered with collodium—Hg	Below 80
" plated " Ag	36-54
" " AgI	59

Mascart found the limiting thickness to be equal to  $140\mu\mu$ ; Vincent, using optical methods in the determination, found it equal to  $160\mu\mu$ . Adadurow,<sup>7</sup> in his study of carriers, attempted to show that unless the catalyst supported by a carrier does not exceed a specific thickness of the layer, it loses its catalytic activity. This catalytic activity may be re-established only by a definite number of catalyst atoms corresponding to a definite number of carrier atoms.

In a series of experiments to determine the change in the number of catalyst (copper) atoms corresponding to a definite number of carrier (carbon) atoms in the aldehyde decomposition of alcohol, Adadurow and Krainyi<sup>7</sup> obtained the following results (Table 15):

Table 15. Aldehyde Decomposition of Alcohol (Adadurow and Krainyi).<sup>7</sup>

—No. of Atoms of— Copper	Carbon	Per Cent Decomposed at				
		250°	275°	300°	325°	350°
2	5	0	0	0	0	0
4	5	0	0	0	0	0
6	5	0	0	0	0	0
8	5	0	0	0	0	0
10	5	0	0	0	0	0
12	5	—	—	—	—	0.43
14	5	—	—	0.48	4.27	6.81
24	5	—	0.78	1.77	8.38	8.44
Pure copper		10.04	22.0	38.2	52.38	84.4

This table shows that a certain number of catalyst (copper) atoms must be present on the carrier (charcoal) before catalytic decomposition of alcohol can take place, *i.e.*, a ratio of 6 atoms of copper to 2.5 surface atoms of carbon.

The depth to which the carrier can be covered is also strongly reflected in the activating ability of the catalyst, as well as in the value of the activation energy, which functions in a catalytic reaction. That the

energy of the external field of a catalyst (copper) deposited on a carrier (carbon) does not remain constant, but changes with the amount of copper deposited, is obvious from Adadurow's calculations of the corresponding activation energies (Table 16).

Table 16. Activation Energies (Adadurow).

—No. of Atoms of—		
Copper	Carbon	Kg./cal.
14	5	37.7
24	5	28.0
32	5	21.0
Pure copper		17.0
(without a carrier)		

The change in the field proceeds gradually, and the decrease in the distortion of the field is inversely proportional to the increase in the number of copper atoms corresponding to one surface atom of carbon. It is assumed that the smaller the energy of the external field of active centers of copper deposited on carbon atoms, the greater the activation energy. With an increase in the amount of copper deposited on the carrier (similar to the surface of pure copper), the heat of activation approaches that of pure copper. Therefore, the amount and concentration of both catalyst and carrier are important factors in securing an effective action of a supported catalyst. Sabalitschka, studying the adsorption of hydrogen by palladium deposited on various substances to the extent of 2.5 per cent of their weight, determined the saturation capacity of these carriers, as shown in Table 17.

Table 17. Adsorption of Hydrogen by Palladium (Sabalitschka).

Carrier	Amount Adsorbed (cc./gr.)
Blood charcoal	1.35
Beech charcoal	0.94
Sponge charcoal	0.84
Bone charcoal	0.72
Barium sulfate	0.60
Kieselguhr	0.26

A saturation point of a rigid carrier for each particular deposit or concentration of the catalyst has been suggested. Griffith,<sup>45</sup> using various concentrations of the carrier in the dehydrogenation of Decalin, decane and hexane over chromium oxide catalyst precipitated on a carrier, found that a greater amount of the carrier may be added in the case of the larger molecules, Decalin and decane, while for hexane, an immediate dilution effect sets in (Figure 1). Griffith explains this action by stating that hexane molecules reach all the active parts of the pure catalyst, which is not the case with either decane or Decalin, or both, since the latter have a pronounced steric effect.

There are cases, such as the oxidation of methyl alcohol on Alundum as a carrier, which suggest the use of varying proportions of the catalyst at different points throughout the carrier columns, with subsequent increase in the content of the catalyst (copper). Similar processes are hydrogenation with reduced nickel, in which the reacting components first pass through a carrier containing small amounts of catalyst; a gradual increase

in the carrier content is considered advantageous.<sup>100</sup> Charmadarjan and Brodowitch<sup>4, 27</sup> studied the influence exerted by carriers on catalysts, particularly with reference to the contact property of catalysts. Carriers recommended for vanadium pentoxide as catalyst in the oxidation of sulfur dioxide were manganese dioxide, asbestos, infusorial earth, quartz, porcelain

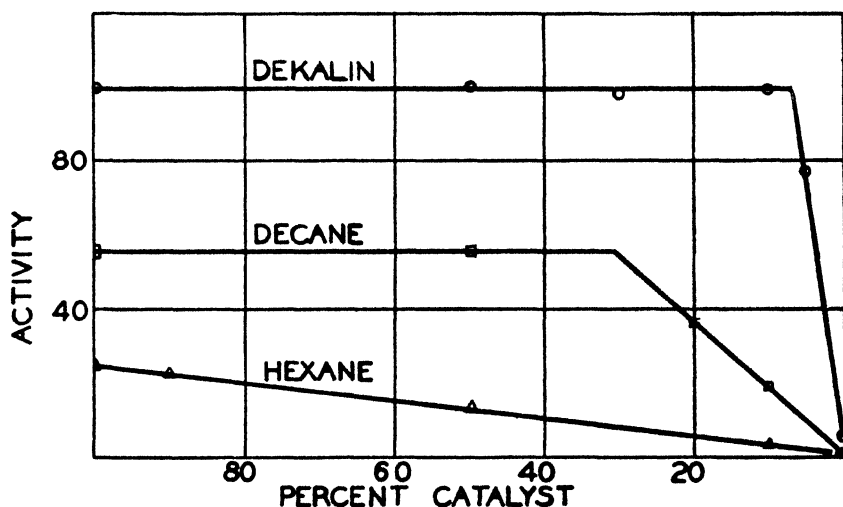


FIGURE 1.—Effect of Carrier Concentration on Chromium Oxide Catalysts.

and glass; manganese dioxide, a catalyst for the contact process in the manufacture of sulfuric acid, gives the best results.<sup>78</sup>

Table 18. Contact Property of Manganese Dioxide.

Temp. (°C.)	Per Cent
450	2.94
500	8.4
550	18.3
600	Decrease

Furthermore, these investigators related the catalytic properties of vanadium pentoxide to the method of precipitation of the catalyst on the surface of the carrier. Coagulation of a colloidal vanadium pentoxide solution by hydrochloric acid gave for all carriers tested, except quartz, a better catalyst than that obtained by coagulation on boiling; the thickness of the vanadium pentoxide layer also being of importance. One per cent ammonium vanadate supported on carriers, such as glass, infusorial earth, asbestos, and porcelain, showed a poor contact property and resulted in a very low yield of sulfur trioxide. With an increase in the concentration of ammonium vanadate the contact property increases, and the increase depends on the type of carrier used; the extent of contact increased for manganese dioxide, quartz and glass. Certain substances, when added to a catalyst, increase the contact property; for instance, cupric sulfate in-

creases the contact property of vanadium pentoxide when deposited on manganese dioxide, infusorial earth, porcelain, or asbestos, and decreases it when deposited on glass, quartz, or sand. Ferric sulfate, which is less active than cupric sulfate, improves the contact property of most carriers, except asbestos; vanadium pentoxide, when deposited on quartz or sand in the presence of ferric sulfate, shows no contact property. Barium chloride, less active than either cupric sulfate or ferric sulfate, slightly improves the contact property of vanadium pentoxide on infusorial earth, porcelain, or asbestos, and greatly influences it on quartz, sand, or glass. Aluminum sulfate is an excellent activator for vanadium pentoxide on manganese dioxide, increasing the contact property up to 97.8 per cent, but is a poor activator for all other carriers except glass. Manganese sulfate is also a good activator for vanadium pentoxide on manganese dioxide.

### Characteristics of Carriers and Methods of Depositing Catalysts on Them

There are certain methods of depositing catalysts on carriers, which vary with the nature of the carrier, as well as with the type of catalyst to be supported. An important factor in the choice of a carrier is whether the catalyst is precipitated or electroplated on the surface of a carrier in order to obtain a more uniform coating, or whether the catalyst is deposited by permeating or impregnating the internal surface of the carrier so that its interior channels or pores, when treated, become covered with a fine precipitate. On the other hand, there are carriers which effect a stable binding with the catalyst layer, thus preventing the catalyst from permeating the interior of the carrier. Impregnating a porous support (colloidal carrier), such as a gel, with a salt solution contributes to the uniform distribution of the reduced metal catalyst throughout the carrier.

*Carbonaceous Materials.*—The adsorption property of wood and bone charcoal has been known for a long time. Lowitz (1785) used charcoal for decolorizing tartaric acid solutions and Fignier (1811) found that bone charcoal likewise possessed marked decolorizing ability. The adsorptive and catalytic properties of variously prepared active charcoals of plant and animal origin vary, depending on the size of pores and the content of foreign substances. Structure and foreign substances also influence the use of carbonaceous materials in catalytic reactions. Some activated charcoals may serve as adsorbents for gases and liquids and, to a limited extent, as catalysts. For example, in the presence of oxygen, some kinds of charcoal oxidize hydrogen sulfide readily; others oxidize carbon monoxide. Many charcoals are suitable for chlorination, reduction, dehydrogenation and polymerization. The behavior of silica gels and zeolites is similar. Permeability and penetrability are other factors to be considered in using carbonaceous materials as carriers for catalysts because of the probability of liquids passing through or being sucked into the porous body. In the case of non-activated charcoal, the openings of hollow spaces or capillaries are closed by skins composed of oriented, saturated atoms. Usually, such skins originate during the coking process and are obtained from adsorbed tarry substances. In the case of activated charcoal, the hollow spaces form

a system comprising one unsaturated active carbon atom placed between twelve inactive carbon atoms.<sup>89</sup> Different kinds of carbon have different sized pores. For example:

Carbon	Macropores	Micropores
wood charcoal	1.2 mm	<0.1 mm
cocoanut shell	0.18 mm	0.28 mm

There is a close relationship between mechanical properties and surface phenomena. By pressing together pulverized charcoal, varying in size of grain, a different type of solidity results, that is, the smaller the size of grain the more solid the body of charcoal particles.<sup>57</sup>

The absorption capacity of charcoal, in its various forms, greatly exceeds that of other substances. It varies not only with the nature and pretreatment of the charcoal, but also with the type of substance to be adsorbed. The adsorption ability of a liquid depends upon its compressibility. Ether, which is much more compressible than water, assumes inside of wood charcoal a volume which is only one-tenth of that taken up by water. Harkins and Ewing,<sup>49</sup> working with degassed cocoanut oil, concluded that liquids penetrating the pores of charcoal are compressed through the action of a force attributed to a molecular attraction, and equivalent to a pressure of several thousand atmospheres. Inorganic electrolytes are normally adsorbed on charcoal, the anion and cation being adsorbed almost to the same extent. This adsorption is weak, amounting to about 0.01 to 0.5 millimol per gram of the adsorbent. Large molecules, such as organic electrolytes, are readily adsorbed by charcoal. If charcoal is distributed between two immiscible hydrophobic liquids, it is better wetted by organic liquids than by water or aqueous solutions. When carbonaceous carriers are used with a precipitated catalyst in hydrogenation or dehydrogenation processes, loss of activity often results; this may be offset by the use of air or oxygen. But since this treatment helps only temporarily, it is recommended that activated material, *i.e.*, charcoal subjected to thermal, acid, or gaseous treatment, be used. Because of the high adsorptive forces, the carrier acts as a depoisoning agent.

Oshima, Fukuda and Ishimura<sup>79a</sup> studied activation of carbon-containing substances such as soot, sugar charcoal, and charcoal from wool fabrics by moist oxidation. The substances were subjected to 8–40 hrs. oxidation with  $\text{HNO}_3$  on a water bath, washed with boiling water, and dried at 100° ( $\alpha$ -charcoal). The insoluble oxidized substances may be removed from the product by thermal decomposition, for example, by heating to 950° in a time interval of 7 minutes ( $\beta$ -charcoal). In order to compare the adsorption isotherms of the starting charcoal,  $\alpha$ - and  $\beta$ -charcoal was taken at 31° with water and benzene vapors. The results obtained indicate that the activation process depends on many factors, such as duration of oxidation, heat treatment, adsorbent, vapor pressure and initial substance. A difference in the behavior of different adsorbents (hydrophilic and hydrophobic) is particularly noticeable in the case of  $\alpha$ -charcoal. From this, it is deduced that the oxidized residue covering its surface is strongly

hydrophilic and when removed by heat treatment, the surface of the charcoal is set free, causing a change in adsorption.

The following method has been used in the preparation of palladium for the hydrogenation of vegetable oils (one part of palladium to 150,000 parts of peanut oil) [*Ber. deut. pharm. Ges.*, 26, 36-48 (1916) and *J. Soc. Chem. Ind.*, 548 (1916)]. The ignited powdered charcoal is shaken with a 2-per cent solution of palladium chloride in the presence of hydrogen until no more gas is adsorbed, and is then washed and dried. This catalyst is quite stable and is claimed to be very effective for complete hydrogenation of fats. It is stated that this catalyst-carrier is completely separated by filtration without leaving any trace of the metal in the fat, and that it effects hardening of the oil in one operation.

N. V. deBataafsche Petroleum Maatschappij<sup>13a</sup> impregnates carbon with a nickel nitrate solution which is dried and the catalyst-carrier treated at elevated temperature first in a reducing and then in an oxidizing atmosphere.

Wright<sup>119a</sup> prepares a fine dispersion of metals (copper, nickel, cobalt, or zinc), or the oxides of these metals, in an ammonia solution into which carbon dioxide is introduced for the formation of ammonium metal compounds. The porous carrier, for example charcoal, is impregnated with these compounds, the compounds are decomposed at 150°, and then reduced.

To 10-12 grams of active charcoal (Bayer's) suspended in water is added the required amount of an aqueous solution of platinum chloride; the flask is heated on a water bath at 50°C. for several hours, cooled, alkalinized with a concentrated solution of sodium carbonate, and the platinum reduced by the addition of a hydrazinehydrate solution drop by drop while shaking the flask, the amount necessary having been previously determined with potassium permanganate. The platinumized charcoal is left standing for one to two hours, washed with hot water to free it from chlorine and alkali, pressed dry between filter paper, dried over calcium chloride for twelve hours, then charged with oxygen while still in the desiccator and maintained in that atmosphere for two days before using.

Colloidal metals of the platinum group are often deposited on carbonaceous materials.\* Merck [Chem. Fabrik, G.P. 342,094, June 21, 1919 and *J. Soc. Chem. Ind.*, 41, 89A (1922)] suggested depositing metals in a "nascent" state, using gum, dextrin, gelatin, etc., as protective colloids; the by-products are filtered off and the colloid heated for a short time and dried. It is claimed that these catalysts are very stable.

**Silica Gel.**—When a silicic acid sol is coagulated, a gel is formed, containing a large number of molecules of water per molecule of silica. Silica gel has a sponge-like structure with ultramicroscopic capillaries whose average diameter is about 5 $\mu$ . Anderson calculated the diameter of these

\* For methods in the preparation of platinum or palladium catalysts on active charcoal for use in hydrogenation and dehydrogenation reactions, reference may be made to Houben-Weyl: Working Methods II, p. 409; Foster and Brude: *Ber.*, 56, 2245 (1923); Marmich and Thiele: *Ber. deut. pharm. Ges.*, 26, 37 (1916); Ott and Eichler: *Ber.*, 55, 2661 (1922); Mayer and Stamm: *Ber.*, 56, 1426 (1923) and Kaffer: *Ber.*, 57, 1263 (1924).

capillaries from the observed vapor pressures of several liquids. He obtained the following results:

2R for water —5.20  $\mu\mu$

2R for alcohol —5.08  $\mu\mu$

2R for benzene—5.58  $\mu\mu$

The capillary rise may be computed from the formula  $h = \frac{2\sigma}{d_L R}$ , if the diameter of the capillaries in the silica gel is known. For water, this is calculated to be several meters, indicating the tremendous force with which water is drawn into the capillaries.

It is recognized that freshly prepared silica gel is not crystalline; with time, a normal orientation takes place due to a progressive rearrangement of silicon dioxide molecules into crystal lattices.<sup>67</sup> When a silica gel is dried over sulfuric acid, a gradual decrease in the ratio of water to silica takes place, which is reflected in a change in the properties of the hydrogel. It has been found<sup>67</sup> that the ratio of 30 to 40 molecules of water to one molecule of silicon dioxide renders the gel of such a consistency that it can be cut. A ratio of 20 molecules of water to one molecule of silicon dioxide makes the gel fairly stiff; with 12 molecules of water to one molecule of silicon dioxide, the gel may be pulverized; with 8 molecules of water to one molecule of silicon dioxide, the gel shows elastic properties; with 6 molecules of water to one molecule of silicon dioxide, the gel appears dry.

King and Lawson,<sup>64</sup> investigating the rate of adsorption of water vapor on silica gel, showed that it required 3 hours; van Bemmelen<sup>111</sup> reported several months, while Patrick and Cohan,<sup>81</sup> in their study, found that at a temperature of 25° and with a vapor pressure of 4.6 mm., 2 or 3 hours are required to establish an equilibrium between silica gel and water, provided the pressure of the gas present is below 0.5 mm. Therefore, only at this low pressure is the rate of adsorption of water on silica gel independent of the gas, whereas at a higher pressure the rate of adsorption is an inverse function of the pressure and molecular weight of the gas. Patrick and Cohan found that the rate of desorption of the last portions of water is an inverse function of the pressure and molecular weight of the gas present during the adsorption, and that the desorption of the first and larger portion of water is almost independent of the gas present.

Regarding the properties of silica gel\* as a catalyst carrier in catalytic reactions, Tschufarow, Tatijewskaja and Kulpina<sup>109</sup> established that the activity of a vanadium catalyst in the oxidation of sulfur dioxide depends to a great extent on the porosity of the silica gel on which the catalyst is supported. When the porosity of the silica gel is increased from 20 to 87 per cent, the yield of sulfur trioxide at 480° increases from 30 to 97 per cent. It is believed that with an increase in porosity a change in the working surface of the catalyst and a more rapid diffusion of the reacting gas molecules takes place, resulting in an increase in the reaction velocity. The activation energy calculated for temperatures above 430° was found to

\* Refer also to (4a) "Short Review of Properties of Silica Gels as Catalyst and Carrier for Catalyst."



be 21,500 calories per molecule, while for lower temperatures, 46,000 calories per molecule.

The most important factor in the preparation of active catalysts supported on silica gel is the manner in which the catalyst is deposited on the carrier, as well as the pretreatment of the carrier. Certain methods have been suggested.

(a) Deposition of metal oxides and sulfides, as well as pure metals, on porous gels. For example, fragments of dry porous silica gel were soaked in a molar solution of silver nitrate, and then were dried and activated by heating for one hour in a stream of dry air at 150 to 200° which removed all but a small percentage of water. After cooling, a stream of hydrogen sulfide was passed through the gel, filling the capillaries, and the gel then thoroughly wetted by water. The hydrogen sulfide and the silver nitrate both dissolved and interacted to form silver sulfide,  $2\text{AgNO}_3 + \text{H}_2\text{S} \longrightarrow \text{Ag}_2\text{S} + 2\text{HNO}_3$ . The distribution of the two reactants in the capillaries of the gel, with the formation of a metal sulfide, is the principal feature of this method. Sulfides of lead and copper, as well as other metals, may be deposited in a similar manner. This method may be applied also to the uniform deposition of metal oxides. A porous gel is immersed in a solution of ferric chloride, dried, activated, allowed to adsorb ammonia and then wetted by water, the ammonia reacting with the water to form ammonium hydroxide, which in turn reacts with the ferric chloride to form ferric hydroxide,  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH}$  and  $3\text{NH}_4\text{OH} + \text{FeCl}_3 \longrightarrow \text{Fe}(\text{OH})_3 + 3\text{NH}_4\text{Cl}$ . In gas catalysis, these metal oxides supported on a silica gel or other porous solid are readily reduced to metals in a stream of hydrogen.

(b) Deposition of metals in a "nascent" colloidal state. Platinum is deposited on silica gel by dipping the carrier in a slightly basic solution of its salts, such as sodium platinate, drying at 100°, and moistening with a formaldehyde solution after cooling; an excess of formaldehyde washes out the platinum salts. The reduction by formaldehyde proceeds slowly at room temperature. When the two reagents mix throughout the porous carrier and the temperature is increased to about 100°, a reduction to metallic platinum in the capillaries of the silica gel takes place. Instead of formaldehyde, sodium formate, hydrazine, tartaric acid, and similar reducing agents may be substituted. Palladium chloride should not be in the form of a basic solution when used for the deposition of palladium. Silver is deposited by immersing the dry gel in a silver nitrate solution of the required concentration, drying below 140°, cooling, and allowing the adsorption of ammonia gas to form the ammoniacal silver complex used in the reduction of aldehyde. The gel is then moistened with formaldehyde solution, heated to 100° to effect rapid reduction, and the silver-coated gel washed with hot water and dried.

The following additional methods for the preparation of silica gel as a carrier have been proposed. Snelling,<sup>100</sup> in connection with the preparation of a siliceous carrier for metal oxides, states that a catalyst of high reactivity results when metal formates are heated, whereby reduction takes place at a very low temperature. Palladium deposited on highly active silicic acid gel prepared by reduction with hydrogen is described in *Berichte*, 56,

2245 (1923). Berl and Urban<sup>18</sup> precipitated a sodium silicate solution with hydrochloric acid, forming a gel which was washed with water to remove all traces of chlorine and then dried in a desiccator over phosphorus pentoxide. Hydrogen is introduced into a suspension containing 20 grams of silica gel and 0.4 gram of palladium chloride solution, to which is added from time to time and drop by drop diluted ammonia to effect neutralization; after this it is washed with water to free it from chlorine and dried, first over phosphorus pentoxide in a desiccator at room temperature and then in the atmosphere at 60°. Brown<sup>21a</sup> mixes gelatinous nickel hydroxide with a sodium silicate solution and prepares silicon oxide gel by adding a quantity of acid sufficient for its precipitation, but not enough to dissolve the nickel hydroxide. The two gels are mixed and calcined to precipitate nickel oxide, which is then reduced.

Reyerson and Thomas<sup>85</sup> impregnated a dry silica gel with a copper nitrate solution, evaporated the mass to dryness, and then reduced it to form the metal by using a stream of hydrogen. Reyerson obtained by reduction with adsorbed hydrogen a uniform coating of silica gel with platinum, palladium, silver, and other metals, the silica gel being completely evacuated at a temperature of -30°, and hydrogen readsorbed on the carrier. The amount of hydrogen adsorbed previous to treatment with a solution, *e.g.*, of silver nitrate, is very marked; with an increase in temperature, a coating of metallic silver is uniformly deposited throughout the gel.<sup>75</sup> Silica Gel Corporation<sup>97a</sup> impregnates highly porous gels (silicon dioxide, tungsten oxide, aluminum oxide) with a catalytically active metal or its compound by charging them with a gaseous reducing compound (sulfur dioxide, carbon monoxide, hydrogen sulfide) and treating with a solution of a metal compound (platinum, silver, copper, palladium, iron).

I. G. Farbenindustrie A.-G.<sup>65</sup> prepared supported catalysts by mixing silicon oxide, aluminum oxide, or ferric oxide in the form of a gel or a sol with the catalytic substance. Silica Gel Corporation (Patrick)<sup>97</sup> prepared silica gel from intermediate hydrogels impregnated with one or more catalysts previous to treatment with dilute alkali. Patrick's silica gel "Monox" was obtained by treating silicon tetrafluoride with water, alumina, stannic oxide or tungstic oxide. A porous mixture of hydrated ferric oxide and hydrated silica may be prepared by the interaction of solutions of sodium silicate and ferric chloride, followed by drying and activation of the precipitate.

General Zeolite Co.<sup>43</sup> (E.P. 313,206) states that the silicon content of a gel prepared from an alkali solution of aluminum oxide and aluminum silicate in the presence of an acid varies, depending on the amount of acid and silicate added. Holmes<sup>64</sup> suggested treating gels having microscopic and ultramicroscopic pores with an impregnating solution. The gel is then heated, first at temperatures at which the reaction is retarded, and then at temperatures at which decomposition of the solution is effected. In this way platinum and silver are precipitated on the walls of the pores of the gel. Silica Gel Corporation<sup>98a</sup> disclosed a method for preparing a catalyst-carrier in which a metal is treated with a salt solution of another metal lower in the electromotive series, effecting an ion exchange and replacement

of the first by the second metal. The dehydrated silica gel is set free from gas saturated with hydrogen in a vacuum at  $0^{\circ}$ , and then treated with a nickel nitrate solution. The nickel compound is reduced and the gel afterwards treated with a silver nitrate solution; thus an ion exchange between nickel and silver takes place. The gel is then dried in the usual manner. E. I. Du Pont de Nemours and Co.<sup>37a</sup> prepare porous catalysts by impregnating a porous carrier of silicon dioxide gel (substantially free from adsorbed gases and liquids), while maintaining a vacuum. The silicon dioxide gel is treated in a vacuum at  $400^{\circ}$ , then cooled and impregnated with a solution of aluminum nitrate, dried and heated again to  $400\text{--}450^{\circ}$ . Budnikoff<sup>24</sup> proposed a method for the deposition of platinum on a silica mass obtained as a residue by removal of aluminum chloride from kaolin. According to this method, a solution of platinum chloride is suspended in turpentine which has been previously treated with sulfur chloride. This method facilitates the preparation of platinum chloride solutions of the required strength. Stable, thin layers of platinum catalyst are deposited on the surface of a carrier with relatively little penetration of the metal into the pores of the carrier. Silica Gel Corporation<sup>98</sup> prepared a silicic acid hydrogel as a carrier for vanadium catalyst by treating it with a solution of a hydroxide compound in a concentration exceeding 0.25 per cent by weight, afterwards bringing it into contact with an excess metal salt solution and drying. The precipitation of catalysts so as to form strips of compounds of the same metal, but of various valences, was recommended.

Westfälische Anhaltische Sprengstoff A.-G. prepare a platinum catalyst on silica gel-carrier, simultaneously with the catalyst, by impregnating it with a solution of magnesium sulfate or aluminum sulfate, or both, then drying and heating to about  $350^{\circ}$ , at which temperature the sulfates of magnesium and aluminum are not converted into the corresponding oxides.

Adadurow, Budnikow and Rjabchenkow<sup>5</sup> proposed the use of substances obtained by the separation of aluminum chloride from kaolin. These substances are stable, porous masses crystalline in structure (crystalline grains, one thousandth part of a mm. in diameter), containing a small amount of quartz and hematite (crystalline grains, 0.08 mm. in diameter). This carrier had the following composition:

Compound	Per Cent
Silicon oxide.	88-96
Aluminum oxide.	12-14
Ferric oxide.	Trace
Calcium oxide.	Trace
Silicon oxide (active).	12.5*

\* Determined by the soda method.

Silica gels, although possessing advantages over asbestos, magnesium sulfate, or ceramic materials, do not find ready application where there is danger of poisoning by water vapor. In this case destruction of the silica gel (contact mass) takes place; it disintegrates, making the passage of gases difficult, and carries away the platinum catalyst supported on it.

*Silicates.*—Silicates differ from other inorganic salts with respect to the manner in which the ( $\text{SiO}_4$ ) groups are linked together to form the silicon-oxygen complexes. In contrast to the carbon-carbon linkage, any linkage

between two silicon atoms in a silicate compound is always effected through an intermediate oxygen atom. Silicon occupies an intermediate position between atoms of phosphorus, sulfur and chlorine, which form with oxygen radicals and with metals, such as magnesium and aluminum, continuous ionic lattices. Silicon forms a simple independent group ( $\text{SiO}_4$ )<sup>''''</sup> in orthosilicates, as well as more complex groups represented by the formulas ( $\text{Si}_2\text{O}_7$ )<sup>''''''</sup>, ( $\text{Si}_3\text{O}_9$ )<sup>''''''</sup>,  $\text{Si}_4\text{O}_{12}$ <sup>''''''''</sup> and  $\text{Si}_6\text{O}_{18}$ <sup>''''''''''</sup>, which may be regarded as complex acid radicals linked by metal atoms as in a salt. Complex silicon-oxygen groups differ in their spatial extensions. Successive spatial extensions represent successive decreases in the oxygen-silicon ratio as follows:

Formula	Group	Characteristic	Oxygen-silicon Ratio
$\text{SiO}_2$ or $(\text{SiAl})\text{O}_2$	hydrous silicates.	three-dimensional net work (zeolites).	
$\text{SiO}_4$	orthosilicates.	tetrads.	1 : 1
$\text{Si}_2\text{O}_7$	metasilicates.	long chains.	2 : 1
$\text{Si}_3\text{O}_9$	polysilicates.	complex groups.	3 : 1
$\text{Si}_4\text{O}_{12}$	disilicates	sheets (mica-like minerals).	4 : 1

Bragg<sup>21</sup> characterized a silicate "as a structure having a constant number of oxygen atoms in the unit and a constant number of places for metal and silicon which can be filled by these elements in varying proportions consistent with a balance between valences." In the case of silicates of alkaline earths, conditions are more favorable for the formation of orthosilicates than for metasilicates (orthosilicates crystallize more readily than the corresponding metasilicates). The fact that orthosilicates crystallize first, followed by metasilicates, may be attributed to a structural difference between these two groups of compounds.<sup>60</sup>

Many silicates are used as supports for catalysts. The following is one of a large number of examples describing the preparation of a silicate as a catalyst carrier. The Compagnie Internationale pour la Fabrication des Essences de Pétrole<sup>31</sup> disclosed a method for preparing aluminum silicate: the mass consisted of an activated aluminum silicate mixed with 30 per cent of plastic silicate; the mixture was washed with water to remove the sodium sulfate formed, and the resulting mass was then shaped into rings and dried. Spence and Sons, Ltd.<sup>100a</sup> describe a method of preparing a catalyst-carrier which involves treating naturally occurring hard aluminum silicate or that hardened in the form of sticks, or grained with a mineral acid, such as sulfuric acid, and impregnating the porous residue with titanium oxide or a platinum salt.

**Zeolites.**—Zeolites are hydrous silicates occurring as natural minerals in volcanic rocks, often in the form of large crystals. Natural zeolites are divided into two classes:<sup>41</sup> (a) those containing alkaline earths or alkalis combined with silica, "double aluminum silicates," and (b) those containing bases combined with alumina, *i.e.*, "aluminum silicates." Zeolites of the first class exchange their bases only to a slight extent and for a short time, while the bases of zeolites of the second class are readily and completely exchanged. Artificial zeolites, "aluminum silicates," prepared by melting together suitable substances and extracting the melted products, are likewise base-exchanging substances, although they are not so readily crystal-

lized. Artificial zeolites are marketed under the trade name "Permutite" described in British Patent No. 23,706.<sup>12, 19, 96</sup> Sodium zeolite is known as "sodium Permutite." Manganese Permutite filters are used for complete removal of iron compounds dissolved in water. Calcium Permutite extracts potassium and sodium carbonate from sugar solutions, requiring no dilution of the material filtered. Potassium carbonate is exchanged not only for calcium oxide (lime) when calcium aluminum silicate is used, but also for sodium in the use of sodium aluminum silicate. An x-ray investigation shows that the process of exchange, when carefully carried out, leaves the crystal lattice unchanged. Only a minimum contraction and expansion of the lattice is indicated by the parameters. To all intent, the crystals appear to be intact, transparent, and without cracks. The zeolite lattice has been found to be constructed of a rigid framework composed of  $\text{SiO}_4$  and  $\text{AlO}_4$  anions. This is a *giant* anion structure. In this framework are channels whose diameters are such that they admit cations, water and molecules of substances of a convenient size. These molecules are not located at random, but occupy definite positions. Water molecules appear to be very closely associated with the cations of the structure, and their arrangement is assumed to be similar to that of hydrous calcium sulfate, or gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

Among the zeolites are scolecite and natrolite which, according to Milligan and Weiser's<sup>73a</sup> x-ray diffraction analysis, may be considered as definite hydrates, whereas others, such as heulandite, thomsonite, analcite, mesolite and chabazite, show no indication of hydrate formation. Stilbite and heulandite exist in more than one modification, and may be hydrates. Some zeolites, after a prolonged or excessive isobaric dehydration, show a definite lattice shrinkage. Therefore the water, as stated by Milligan and Weiser (14th Colloid Symposium, Minneapolis, June 10-12, 1937) is not always held in a manner similar to the hemihydrate of calcium sulfate.

Zeolites are adsorbents and as such are characterized as being suitable for the adsorption of molecules of a certain size; on the other hand, they are also suitable for the adsorption of small molecules of substances readily volatilized. By heating in a vacuum, zeolites may be freed completely from foreign substances and thereby readily regenerated.<sup>105, 107</sup>

Zeolites, used as carriers in catalytic reactions, consist of a base-exchanging polysilicate in which the catalytically active elements may be present in the nucleus of the zeolite. These elements may be present also in a non-exchangeable form or, as exchanging cations of the zeolite, may constitute an anion forming a salt-like body with the zeolite; then again, they may be simply mixed or impregnated with a diluent used together with the active zeolite. The nature and proportions of the active materials may be varied, to render the catalyst suitable for use in the oxidation of any volatile organic compound by air in a vapor phase.

There are various methods for incorporating catalysts in zeolites. Mittasch, Schneider and Morawitz<sup>74</sup> prepared a platinum zeolite for the hydrogenation of organic compounds by heating an artificial zeolite until nearly all the water was driven off, soaking it in a solution of platinum

hydrochloride, and then drying and reheating; thus any soluble salt, such as sodium chloride, can be removed by washing or digesting. The introduction of platinum and osmium metals into the silicate can be effected by digesting the alkali metal, aluminum silicate, with a solution of a platinum metal salt. An osmium zeolite is usually prepared by soaking the zeolite in a solution of potassium osmate and heating. Artificial or natural zeolites are first converted into an ammonium zeolite after which, either directly or after preliminary heating, it forms osmium zeolite by treatment with potassium osmate. For other methods regarding the preparation of base-exchanging products, refer to Selden patents.<sup>94</sup> Zeolites of the aluminum silicate or double aluminum silicate type used in the reduction of carbonyl compounds as catalyst carriers are described by Selden (F.P.).<sup>94</sup> Base exchangers are prepared by the action of an alkali solution of aluminum oxide on a solution of an alkali silicate in the presence of an acid and neutralized,<sup>43</sup> the silica content being varied by added amounts of silicate and acid. The end product is treated either before or after drying with sodium hydroxide, sodium carbonate, or sodium acid carbonate.

*Pumice.*—Pumice is a glassy lava, volcanic in origin, and of a cellular texture. In chemical composition, pumice is a complex silicate of aluminum, sodium, potassium, calcium, magnesium and iron. It is a non-oxidizable substance and readily affected by poisons. Pumice as a carrier and an adsorbent is used in various grain sizes.

One of the methods for the preparation of catalysts on pumice was suggested by Brunel<sup>23</sup> who impregnated granulated pumice in a thick paste of precipitated nickelous hydroxide, dried the mass on a water bath, and then reduced the nickel-pumice catalyst in the same tube in which the catalytic hydrogenation occurred. According to deHaen,<sup>46a</sup> 40 grams of nickel formate or freshly precipitated nickel carbonate is stirred into a paste with 20 grams of pea size purified pumice, using water, the mass obtained being heated at 200–280° in a stream of hydrogen until no more water is given off. In another method fine, granulated pumice is impregnated with purified nickel hydroxide which is dried at 140°, and the catalyst-carrier reduced at 270–290° in a stream of hydrogen. Very fine pumice has been suggested as a carrier for nickel, copper, platinum black and platinum oxide.<sup>91</sup> Voorhees and Adams,<sup>115</sup> in their preparation of a catalyst on pumice, recommend suspending platinum oxide in water and adding finely dispersed pumice, the supported catalyst being evaporated to dryness on a water bath. These investigators suggest stirring the mixture during the process in order to avoid the precipitation of platinum oxide on the bottom of the container. Gorris,<sup>44</sup> in the dehydrogenation of ethyl alcohol, used equal parts of aluminum hydroxide and pumice, obtaining 96.6 per cent ethylene and 3.4 per cent hydrogen. Kesting,<sup>63</sup> for the same reaction, used a hydroxide of aluminum prepared from aluminum nitrate precipitated by ammonia, or the unglowed commercial product, alumina (de Haen); he obtained 90 per cent of the theoretical yield. Escourou<sup>39a</sup> uses pumice the size of a pinhead prepared by splitting and sieving. Vanadium pentoxide or other oxidation catalysts are rubbed to a thin paste with pure water, the

pumice particles dipped into the suspension, the catalyst drawn in and then heated.

*Asbestos*.—Asbestos is a variety of amphibole occurring in long and delicate fibers, or in fibrous masses or seams, usually of a white, gray, or green-gray color. Another variety of asbestos is altered serpentine, which is a mineral or a rock consisting essentially of a hydrous magnesium silicate,  $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$ , and usually of a dull green color, often resembling a spotted or a mottled appearance, like a serpent's skin. The presence of iron may give it a red or brownish hue. It usually occurs in masses, which are sometimes foliated, sometimes fibrous. The fibrous silky variety of serpentine is called "chrysotile"; it is flexible and elastic, and has high tensile strength. Serpentine results from the alteration of other magnesium minerals, especially chrysolite, amphibole, and pyroxene, and is frequently found in large masses. Chrysolite is a magnesium iron silicate, usually olive green, occurring in orthorhombic crystals, in masses and in grains, and common in certain igneous and metamorphic rocks; it is also called olivine. Amphibole is a silicate of calcium and magnesium and usually one or more other metals, such as iron, manganese, etc. It is monoclinic and includes many varieties differing in color and composition. Amphibole is a component of many crystalline rocks. Some of the non-aluminous varieties are tremolite, actinolite and richterite (including nephrite and asbestos); edenite and common hornblende represent the aluminous type. Pyroxene is a common monoclinic mineral, usually occurring in short, thick, prismatic crystals of square cross-section or in massive forms, often laminated. It varies in color from white to dark green and black and even blue. Pyroxene is a metasilicate, composed chiefly of calcium and magnesium, and includes many varieties, some aluminous and others containing little or no aluminum. Anthophyllite is another type of asbestos; it is an orthorhombic mineral of the amphibole group, is often clove brown in color and lamellar or fibrous. Anthophyllite is a brittle fiber, of low tensile strength, but more resistant to acids and heat than chrysotile. It is essentially a silicate of magnesium and ferrous iron,  $(\text{Mg}\cdot\text{Fe})\text{SiO}_3$ . The amphibole group is a group of minerals closely allied to the pyroxene group and paralleling the latter in composition, but differing in cleavage, crystalline form, etc. Amosite, another form of anthophyllite, is rich in iron. Tremolite is a white or gray variety of amphibole occurring in long, bladelike, or short, thick crystals, and also in columnar, fibrous, or granular masses. It is essentially a calcium magnesium silicate,  $\text{CaMg}_3(\text{SiO}_4)_3$ . Actinolite is a bright or grayish-green variety of amphibole containing calcium, magnesium and iron,  $\text{Ca}(\text{MgFe})_3(\text{SiO}_4)_3$ , and occurs often in fibrous, radiated, or columnar forms. Hornblende, the common black, dark green, or brown variety of aluminous amphibole, contains considerable iron and occurs as distinct crystals, as well as in columnar, fibrous and granular forms. Crocidolite, "blue asbestos," is a lavender-blue or leek-green mineral of the amphibole group occurring in silky fibers, and also in massive and earthy forms. It is flexible and elastic, with a tensile strength greater than that

of chrysotile. Crocidolite is essentially a silicate of iron and sodium,  $\text{NaFe}(\text{SiO}_3)_2\text{FeSiO}_3$ .

The silicon oxide content in asbestos ranges from 40.36 to 58.80 per cent, depending on the type. A summary of averages is given in Table 19.

Table 19.

Compound	Per Cent
$\text{Al}_2\text{O}_3$	0.21- 5.72
FeO	0.66-37.00
MgO	2.30-43.86
CaO	0.5 -10.65
$\text{H}_2\text{O}$	0.5 -13.45

Some of the characteristic properties of asbestos and related substances to be considered when used as carriers for catalysts are the following:

(1) The fibrous structure, due to a highly developed prismatic cleavage. Fineness of fibers is measured by the degree of separation of fibers. Anthophyllite fibers measure as low as 0.002 mm. in diameter. Cirkel<sup>29</sup> claims having determined the smallest measurable diameter, 0.00075 mm.

(2) Heat resistance: suitable as fireproof material. The Canadian variety of chrysotile withstands temperatures ranging from 2000 to 3000°F.; some other varieties withstand temperatures up to 5000°F.

Only at high temperatures is the water of crystallization of asbestos driven off, rendering the substance brittle. Regarding the percentage of water in asbestos and related types, anthophyllite, tremolite and amosite have a low water content; crocidolite also has a low water content, but is readily fused into a black magnetic mass. Asbestos, in general, is considered non-inflammable and serves as a heat insulator.

(3) Certain varieties of asbestos, such as tremolite and anthophyllite, are not affected by acids, while others, such as chrysotile, are less resistant to chemicals, particularly acids; crocidolite is especially resistant to chemical action.

(4) Electrical resistance is shown best by those types of asbestos which are low in iron. Arizona chrysotile is considered as showing great electrical resistance. Although crocidolite has a high percentage of iron, it is highly resistant electrically; however, this is not considered contradictory to the above, for the iron is, in this case, in the form of a silicate.

Wesson<sup>117</sup> and Woodruff<sup>119</sup> recommend impregnating asbestos with a catalyst by dissolving nickel nitrate in water and adding ammonium hydroxide to form nickel hydroxide; the voluminous flocculent precipitate is then mixed with the inert carrier, asbestos. Zelinsky and Borisoff<sup>120</sup> state that a uniform distribution of palladium throughout asbestos can be obtained by impregnating asbestos with a concentrated solution of palladium chloride and reducing with formalin. The asbestos, which has been purified by washing with acid, is glowd and then impregnated with an acidified concentrated solution of palladium or platinum chloride. The absorption of the solution by the asbestos and deposition of the metal is brought about by heating the asbestos on a water bath and then adding 35 to 40 per cent of formalin. (One gram of platinum chloride requires 2.5 to



3.0 cm.<sup>3</sup> formalin; one gram of palladium chloride requires 4.5 to 5.0 cm.<sup>3</sup> formalin.) After the metal has been deposited on the carrier, the asbestos is washed with water to remove the salt and alkali, dipped into a weak acetic acid solution to remove the last traces of alkali, drained using suction, washed with water until neutral to litmus and then dried at 110° in an oven for a short period of time. The metal content is about 40 per cent.

Asbestos may be impregnated with osmium dioxide by introducing asbestos, which has been washed with hydrochloric acid and water, into an aqueous solution of osmium tetroxide and heated to glowing. After impregnating and stirring for one hour, a calculated mixture of hydrazinechlorhydrate is added, and also sodium hydroxide, until the solution is alkaline in reaction. After heating for thirty minutes, osmium dioxide is formed as a black precipitate on the asbestos. The supported catalyst is filtered using suction, washed alternately with water and acetic acid, dried for one day at 50° and for several days in a desiccator over sulfuric acid. A very active catalyst with a good hydrogenation surface is obtained. Osmium dioxide is reduced to metallic osmium by hydrogenation.

In depositing iridium on asbestos, ammonium chloroiridate is dissolved in a large amount of boiling water, alcohol added for partial reduction and then the calculated amount of asbestos. When the asbestos is well impregnated, a solution composed of formic acid and sodium or ammonium acetate is gradually introduced into the boiling mixture. The excess solution in the iridium-asbestos mixture is removed by suction, washed with boiling water and dried at 110°. Iridium is activated by blowing a stream of oxygen through it for several hours at 350–400°. <sup>59</sup>

Ssadikow and Michailow<sup>101</sup> showed that better yields (70%) in the hydrogenation products are obtained in the pressure hydrogenation of pyridine if platinum or iridium is substituted for nickel oxide on asbestos as catalyst. Medwedew and Alexejewa<sup>72</sup> claim that osmium dioxide precipitated on asbestos is quite suitable for the oxidation of substances with olefinic bonds. Weber<sup>116</sup> treats asbestos with an acid and a soluble silicate, such as Si(OH)<sub>4</sub>; a soluble salt is thus formed with the acid. A solution of rare earths, from which the oxide is formed, is used as a catalyst. The Peoples Gas Light and Coke Co.<sup>42a</sup> prepare a contact mass for the oxidation of toluene and similar hydrocarbons at 290° by distributing 15 grams of asbestos fibers in a hot solution of 30 grams of ammonium vanadate in one liter of water, and adding slowly 3 cc. of ammonia solution (D = 0.9); to this mixture is added, with strong stirring, a solution of 107 grams of ferrous sulfate in 450 cc. of water. To keep the mixture alkaline, 60 cc. of ammonia solution is poured in. After stirring for one hour, it is filtered, the precipitate washed with a small amount of water and the mixture molded in sticks, dried in an oven and broken into small pieces. The yield is about 40 grams.

*Siliceous Earths.*—Diatomaceous earth, infusorial earth, tripoli and kieselguhr are natural siliceous deposits composed wholly of the shells of diatoms which are microscopic unicellular marine or fresh-water algae, remarkable for the silicified cell wall persisting as a skeleton after the death

of the organism. These substances occur in friable masses, are light, loose and powdery, of a fine and more or less uniform grain, and usually white or gray in color. Diatomaceous earths are used as abrasives and absorbents, for filters, fixation dressings, etc., and readily form pastes.

Porous kieselguhr when burned may be uniformly impregnated with aqueous salt solutions, such as silver nitrate, copper sulfate, *et al.*; during drying these salts have a tendency to move into the upper layer.<sup>15</sup> Diatomaceous earth adsorbs water very readily. Berkefeld filters of the same adsorption rating show variation in their behavior as adsorbents due, no doubt, to the fact that diatoms are crushed differently. Alcohols, such as methanol and ethanol, as well as carbon tetrachloride, are not as readily adsorbed as water. Diatomaceous earth adsorbs sodium thiocyanate less readily than sodium nitrate or sodium sulfate, solutions of which exhibit negative adsorption in a Berkefeld filter.<sup>27, 53</sup>

A number of methods for preparing catalysts on infusorial earth, kieselguhr and other siliceous earths have been recommended. E. I. Du Pont de Nemours and Co. (Gibbs)<sup>37</sup> impregnated infusorial earth with melted vanadium oxide. Haseman<sup>50</sup> made a comparison of the various types of earths. The Verein für Chemische und Metall Produktion<sup>112</sup> patented a catalyst (silicon dioxide or silicate) preparation on infusorial earth. For example, infusorial earth containing a mixture of 10 to 15 per cent ferric oxide and aluminum oxide mixed with precipitated aluminum oxide to which has been added an ammonium salt to render the mass loose and fluffy is heated to form silicates, the basic ingredient of which is removed by treating with a mineral acid. The temperature at which this reaction takes place is dependent on the initial substance used. Nickel precipitated on infusorial earth or florida bleaching earth (fuller's earth) is suggested for fat hardening in hydrogenation processes at ordinary pressure.

Kulkarni and Jatkar<sup>68a</sup> investigated the activation and bleaching ability of fuller's earth. By using the conductivity method, the writers derived the exchange equilibrium between H ions of activated fuller's earth and Na ions of a NaCl solution of various concentrations. The equilibrium constant  $K = (H^+)^2 / (Na^+ \cdot H^+)$  for suspensions with one per cent activated earth was  $1.1 \times 10^{-5}$ ; with 2 per cent activated earth,  $3.0 \times 10^{-5}$ . From the results obtained it has been concluded that, for small concentrations of earth, adsorption effects do not play a marked part and that the exchange  $H^+ \rightleftharpoons Na^+$  follows stoichiometrically. The minuteness of the  $K$  values shows that the  $H^+$  is held on the activated earth much more strongly than the Na ions, and this explains the great action of even dilute acids in the process of activating earths. In practice, however, concentrated acids are used which cause a break-up of the crystal lattice of the earth particles and therefore an increase of the active surface.

Crosfield<sup>34</sup> impregnated kieselguhr with nickel sulfate by treating the carrier with an alkali hydroxide to form nickel hydroxide which is precipitated throughout the porous carrier. The latter is well washed, dried and reduced; the kieselguhr contains about 30 per cent of metallic nickel. Kayser<sup>61</sup> obtained catalysts in a state of fine division as metallic powders

by bringing the carrier, kieselguhr or infusorial earth, into intimate contact with nickel nitrate, nickel oxide, nickel hydroxide, or nickel carbonate, drying, comminuting and reducing the powder formed. I. G. Farbenindustrie A.-G.<sup>56</sup> prepared nickel and cobalt precipitates on kieselguhr. Nickell<sup>79</sup> mixed kieselguhr with water glass, forming a doughy mass which was shaped into balls and dried. The water glass was decomposed by precipitating silicon dioxide with acid. In oxidizing sulfur dioxide to sulfur trioxide, Imperial Chemical Industries<sup>57a</sup> prepared a gelatinous mixture of kieselguhr and an alkali solution precipitated by acid on which silicon dioxide was deposited and dried. Catalysts such as vanadium or platinum or their compounds were deposited on the porous carrier thus obtained.

The Verein für Chemische und Metall Produktion<sup>112, 113</sup> prepared a platinum catalyst with sulfuric acid supported by kieselguhr. Materials having a high silicic acid content were heated with silicates. Freshly precipitated aluminum oxide is used with a silicate to form metal oxides or salts, the basic ingredients being removed from the reaction mixture by treatment with mineral acids (hydrochloric or sulfuric). The activating substances may be deposited on the surface of the carrier either in aqueous or alcoholic suspensions and dried at 60 to 100°. Carriers, such as seafoam or kieselguhr, may be plated with platinum when impregnated with a solution of platinum chloride and dried at 60–100°. Before plating takes place, the carrier is pressed into shape and glowd below 1000°. <sup>10</sup>

*Chamotte.*—This substance is a dead-burned fireclay grog with plastic fireclay as a binder. On account of its adsorption properties, it is well adapted as a carrier. Under certain conditions of preparation, chamotte effects a stable binding between it and the catalyst layer without penetration of the latter into the internal portion of the support.

Chamotte has been recommended as an excellent carrier for silver vanadate, as well as for vanadium pentoxide catalysts. Since direct deposition of silver vanadate is not successful because of a slight covering and a surface distribution which is not uniform, it has been suggested that vanadium pentoxide be precipitated first on chamotte and the vanadium chamotte then treated with a sufficient amount of the silver salt, the ratio of vanadium pentoxide in the catalyst to silver oxide being from 0.86 to 1.7 per cent.<sup>2, 3</sup> Dullberg<sup>36</sup> found that by acidifying a solution of ammonium vanadate two complex vanadium acids are formed, the tetra-*vanadic acid* ( $H_2V_4O_{11}$ ) and the hexa-*vanadic acid* ( $H_4V_6O_{17}$ ). The percentage of vanadium pentoxide deposited is a function of the concentration of the solution. In solutions of low concentration, precipitation by coagulation begins only after a certain period of heating and proceeds slowly, while in concentrated solutions precipitation by coagulation begins immediately and ends abruptly. When using chamotte as a carrier for vanadium pentoxide, it is of importance to apply a solution of a vanadium salt in which hexa-*vanadic acid* is formed, because only this gives on heating a fixed stable vanadium pentoxide precipitate.

Adadurow and Boresskow<sup>2</sup> are of the opinion that the concentration of hydrogen ions is the principal factor inducing coagulation. According to

Hardy's rule, ions charged oppositely to colloids cause their coagulation; therefore the positive hydrogen ions coagulate the negatively charged ions of  $H_4V_6O_{17}$ . Practice indicates that even though hexavanadic acid is acidified and boiled for  $1\frac{1}{2}$  hours, 5 to 20 per cent vanadium pentoxide still remains in solution; therefore the deposition of vanadium pentoxide on chamotte is incomplete. An excess of 16 equivalents of acetic acid used in acidifying does not materially assist the precipitation, while small amounts of mineral acids give the desired result.

The impossibility of complete coagumulation and fixation of vanadi pentoxide on chamotte from vanadate solutions was brought out by Dullberg,<sup>36</sup> who showed that the complex vanadium ion changes its properties with changes in conditions and may be present in the form of an anion as well as a cation at the same time. Adaduwrow and Boresskow deduced therefrom that in the case of a high concentration of the acid the vanadate ion changes its anion properties.

Adaduwrow and Boresskow<sup>3</sup> describe the preparation of a vanadium catalyst and the method by which it is deposited on chamotte. A catalyst consisting of 56.95 per cent vanadium pentoxide, 37.43 per cent ferric oxide and 5.62 per cent water was prepared from ammonium vanadate by adding to its solution an activator, ferric oxide. A light yellow amorphous precipitate, not readily filtered, is formed, which is soluble in an excess of a concentrated solution of ferric chloride, forming a brownish solution. On heating this solution, a precipitate is formed which changes into a light yellow deposit when acidified; in strong acids, this yellow precipitate dissolves readily; in weak acids, it separates on heating and dissolves on cooling. For a dilute solution of the vanadate (1.25 grams ammonium vanadate per liter), a complete dissolution takes place only when 4 to 5 equivalents of a strong acid are added; for more concentrated solutions (10.0 grams ammonium vanadate per liter), 2 equivalents of the acid will suffice and, in the presence of 4 equivalents, the precipitate does not form even upon heating the solution. The catalyst obtained in the form of a powder is stable against a glowing temperature of  $800^\circ$ , bakes together slightly at  $950^\circ$  and melts at about  $1200^\circ$ . The deposition of this catalyst on chamotte is due to its ability to reprecipitate on heating when dissolved in the cold in a few equivalents of strong acids. When such a catalyst solution is heated with chamotte, the carrier assumes a yellow color. Best results are claimed in the use of 4 to 5 equivalents of a mineral acid.

Silver salt as an activator may be substituted for the iron salt. In preparing silver vanadate catalyst on a carrier, vanadium pentoxide is first precipitated on chamotte and then treated with silver nitrate, the action of the free nitric acid formed being retarded by the addition of sodium acetate. The catalyst obtained is stabilized by heating in an electric oven up to  $675^\circ$ .

Charmadarjan and Brodowitch<sup>27</sup> recommend three general methods for the deposition of vanadium pentoxide, namely, (a) coagulation of vanadium pentoxide from a colloidal solution by boiling. The hydrosol of vanadium pentoxide is prepared from a vanadium salt by the addition of a

few drops of dilute hydrochloric acid (Biltz). A definite amount of the carrier is placed in a porcelain dish, and the colloidal solution of vanadium pentoxide is poured over it and boiled. This results in coagulation of the solution and deposition of flaky vanadium pentoxide on the carrier. The solution is evaporated to dryness and dried in an oven at constant temperature ( $140^{\circ}$ ). (b) Coagulation of vanadium pentoxide from a colloidal solution by acids. A definite amount of the carrier is treated with a colloidal solution of vanadium pentoxide, hydrochloric acid added, an instantaneous coagulation effected, and dark, red flakes of vanadium pentoxide are deposited on the carrier. (c) Impregnation of the carrier with a solution of ammonium vanadate. The carrier is impregnated with a solution of ammonium vanadate, stirred constantly to insure uniform distribution of the solution on the surface, the excess solution evaporated and the mass glowd at  $440^{\circ}$  for complete removal of the ammonium salt [*Z. Elektr.*, **34**, 824 (1928)].

*Gypsum*.—Gypsum is the hydrated sulfate of calcium,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , colorless when pure, occurring in the form of monoclinic crystals, easily splitting into folia. It has a hardness of 2, and a specific gravity of 2.31 to 2.32. Gypsum occurs in extensive beds over the world and is used as a dressing for soils, for making plaster of paris, etc. Plaster of paris is a white powdery substance  $(\text{CaSO}_4)_2\text{H}_2\text{O}$  formed by calcining gypsum until it is partially dehydrated. It forms with water a paste which readily sets, and is used for casts, moldings, etc.

It has been postulated by Cavazzi (1913) that the setting process of plaster of paris may be due to a gel formation. Traube sought proof for this explanation in the retarding and accelerating effect of electrolytes (Hofmeister series), but Wo. Ostwald and Wolski<sup>80</sup> proved that the Hofmeister series holds not only for colloids, but for molecularly dispersed systems as well. They also contended that a finely dispersed plaster of paris has a much greater hydraulic effect than one coarsely dispersed. The setting process has been compared with the formation of an anhydride, but Neugebauer<sup>77</sup> found that preparations slowly dehydrated gave normal setting curves, while preparations subjected to double hydration gave setting curves analogous to those of dehydrated plaster of paris containing about 4 per cent of water of crystallization.

Regarding the effect of electrolytes, it was ascertained that potassium chloride solution of low concentration accelerates the setting process, while a high concentration retards it. Organic colloids, such as gum arabic, gum tragacanth and gelatin, similar in effect to alcohol, slow down the setting process. A 0.2-per cent gelatin solution added to a 4-per cent plaster of paris preparation is sufficient to suppress completely the setting process. The binding in the setting process may occur with varying rates of speed, since the rapidity with which gypsum sets is dependent on the fineness of its grain. The transition from the slow-setting to the fast-setting process is sudden.

In a two-component system, the behavior of hydrous  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  and  $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$  is similar to that of cements, since they set in a compar-

atively short time; impurities such as kaolin and bauxite prolong the setting time.

In a three-component system,  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ , which is especially rich in aluminum oxide, hydraulic setting takes place. A fusion of these components at  $1600^\circ$  imparts high mechanical strength to the mass formed. Ordinary cements sinter, rather than fuse. The sintering process induces the formation of a coherent solid mass by heating without thoroughly melting.

*Cements.*—Among the many types of cements produced and marketed are ordinary portland cement and portland cements which contain an active siliceous material, plastic cements, and "high silica" cements, e.g., puzzolan. Tufa cement is also a special cement. Another type, masonry cement, is prepared by grinding calcined calcareous rocks, and is used in brick making.

Portland cement is a hydraulic cement consisting of compounds of silica, lime and alumina. It is so called from its resemblance in color when set to the Portland stone of England. It is variously made of chalk, limestone, marl, clay, slate, river mud and blast furnace slag, and used in such a mixture as to contain lime, alumina and silica in the right proportions. The intimately mixed ingredients are burned in a kiln to incipient vitrification, and the clinker formed is ground to a very fine powder. When this cement is mixed with water, it sets slowly, owing to the interlocking of minute crystals formed. In the presence of an excess of water the products formed hydrolyze, calcium hydroxide passes into solution, leaving more of the siliceous material in a solid state. The addition of water therefore is an important factor in the setting process, since the hydration of portland cement is accompanied by the evolution of heat. In practice, it is recommended that 50 to 75 pounds of water be used for each 100 pounds of portland cement. Hydration products of portland cement withstand a stress of about 5000 pounds per square inch.

Many theories have been proposed regarding the setting process of portland cement. Endell<sup>39</sup> assumed the crystallization of calcium silicate (needle-shaped crystals) and calcium aluminate (crystalline platelets). It is believed that, as the result of a comparatively rapid crystallization, the gel mass consisting essentially of calcium silicate separates, and to this the solidification process is ascribed. So long as calcium hydroxide, silicic acid and water are available in the system, the formation of the gel continues. LeChatelier considered the formation of crystalline needles from a saturated aqueous solution of soluble hydrates essential to solidification, the small amount of water set free dissolving the intermediate anhydrous compounds. Liesegang assumed that water forms a saturated solution and that in solidification the greater solubility of the dispersed phase should be accounted for. Haegermann<sup>46</sup> stated that in the setting of cement, crystals of monopotassium silicate and tricalcium aluminate are formed, the excess water present decomposing them hydrolytically, while calcium hydroxide passes into solution, and silicon oxide and aluminum hydroxide, which adsorb calcium oxide from the solution, precipitate as gels. It has been emphasized by Traube<sup>108</sup> and by Kühl<sup>68</sup> that in the process of solidification a colloid is formed which gradually changes into a microcrystalline mass.

Wo. Ostwald compared this process to the swelling of organic colloids in which a part of the water is given off to the silicate gel formed. A chemical theory for the setting of cement proposed by Benson, Newhall and Tremper<sup>17</sup> assumed that substances present give, with calcium hydroxide and other compounds of the cement, insoluble reaction products.

In general, cements have very definite physical characteristics; that is, they are plastic, have high tensile strength, give off little heat in hardening, are impermeable, and resist chemical treatment. For example, hydraulic alumina cement has high tensile strength in the early stages of setting. The International Cement Corporation<sup>58</sup> patented a method for the preparation of a portland cement which hardens very rapidly. A mixture of raw portland cement containing an excess of free lime is burned and the clinker formed reduced to a fine powder; particles containing an excess of lime are removed. It is claimed that the product obtained is a useful form of cement.

*Clays.*—Clay is a widely distributed earth, plastic and tenacious when moist and hard when baked. It consists of pure kaolin or, more commonly, of a mixture of kaolin with more or less finely eroded material, chiefly quartz, feldspar and mica, and is the result of the decomposition of granite and similar rocks. Dry clay consists essentially of a compound of alumina (39.53 per cent), silica (46.52 per cent) and combined water (13.95 per cent). When it is subjected to a baking heat, water is formed which passes off as steam, and a material quite different from the original clay is left behind. It is very hard and its powder, when mixed with water, is not plastic. A change of color may also take place; for example, some clays redden, due to oxidation of the iron compounds contained in them.

In general, two types of clays are recognized: (a) primary clays, such as kaolin, and (b) secondary clays, such as ball, shale, glacial, alluvial and flint clays. Kaolin is the purest form, and is used not only for the manufacture of porcelain, but also as a source of aluminum metal. It is a hydrous silicate of aluminum,  $H_4Al_2Si_2O_9$ , and is derived from the decomposition of aluminous minerals, especially feldspar. Pure kaolin fuses at  $1750^\circ$  and has a hardness of 2.0–2.5. Impure clays melt at a temperature as low as  $1100^\circ$ . Impurities changing essentially the properties of clays are feldspar, iron oxides and calcium carbonate. Ball clay is sticky, has a tendency to form balls, and is used as a pipe clay. Shale is a rock formed by the consolidation of clay, mud, or silt, having a finely stratified or laminated structure. Glacial clay is icelike in form; alluvial clay relates to deposits made by flowing water. Flint clay is a hard, flintlike variety of fireclay, or other highly siliceous material, which is capable of being subjected to high heat without fusion. Electrolytes coagulate or deflocculate clays as the result of a chemical reaction, coagulation resulting from a decrease in the electrical charge, while deflocculation results from an increase in the electrical charge. For example, the addition of an acid converts the negatively charged particles into positively charged particles, which results in coagulation. The valence of the adsorbed ion is an important factor in coagulation. As a class, clays are acid in reaction, the pH ranging from 3.10 to 7.27; the isoelectric point lies between pH 2.7 and 4.0.

The addition of lithium, sodium, and potassium increases the negative charge and results in deflocculation. Maximum deflocculation for clay compounds varies from pH 11 to 12. Sulfates of calcium and aluminum retard deflocculation. It is a recognized fact that clays containing organic colloids deflocculate more readily than those which do not contain such substances.

The adsorption ability of clays having basic ions is especially noticeable. Bencke<sup>16</sup> found that one gram of kaolin adsorbs 0.0038 to 0.016 gram of copper oxide from a 4-per cent copper sulfate solution. Arrhenius ascertained that clays adsorb dyestuffs in proportion to their molecular weight. Since the adsorption ability of clays is related to the fineness of their grain, it is important to determine the size of clay particles.

Various methods have been proposed for determining the size of particles. Seger determined the size of grains of clay compounds measuring 0.010 to 0.005 mm. in diameter by utilizing the velocity of a current of water flowing at 0.18 mm. per second. Stark<sup>102</sup> recommends mixing clay with water and placing it over a 3-per cent sugar solution. The size of particles is computed from Stokes' formula:  $r = \frac{\sqrt{9KC}}{2(S_k - S_l)}$ , in which  $r$  denotes the radius of the clay particles;  $K$ , the viscosity of the liquid;  $C$ , the rate of sedimentation;  $S_k$ , the specific gravity of clay, and  $S_l$ , the specific gravity of the liquid.

Fractional sedimentation has been carried out on two types of clay: (a) Zettlitz kaolin and (b) plastic bond clay, with the following results (Table 20):

Table 20.

	Zettlitz Kaolin	Plastic Bond Clay
Average diameter.	4.8%	3.6%
Coarse particles (11-49 microns).	32.0%	21.0%
Number of particles per gr.	$6.6 \times 10^9$	$15.8 \times 10^9$
Specific surface in sq. cm.	4810	6410

The grain size of clay substances has been expressed also by means of a surface factor according to the formula:

$$S = p_1^1/d_1 + p_2^1/d_2 + p_3^1/d_3, \text{ etc.}$$

in which  $S$  is the surface factor;  $p_1$ ,  $p_2$ , and  $p_3$ , the fractional parts of the different sized portions, and  $d_1$ ,  $d_2$ , and  $d_3$ , the mean diameter in each portion.

Another property to be considered in the use of clay as a carrier is its permeability to water or aqueous solutions. It is stated that the permeability of clay to water varies as  $K/r^3$ , where  $K$  is a constant and  $r$  the mean radius of the particles. Thoroughly dried clay readily adsorbs moisture; the amount of water adsorbed is assumed to be proportional to the amount of colloidal material in the clay, and inversely proportional to the mean diameter of its particles. The proportion of adsorbed water has been estimated to be as high as 6 per cent. Depending upon the original moisture content, the amount of water in the pores corresponds to the amount of



water remaining in the clay; hygroscopic plastic clays may show a shrinkage of 10 to 35 per cent. If the rate of surface evaporation from clay containing a large amount of water retained by its colloidal constituents is greater than the water content within the substance itself, cracking of the clay may result. The dehydration of clays heated to about 225° is attributed to loss in hygroscopic moisture.

Dehydrated clays are very active chemically, combining with alkalis and with the hydroxides of the alkaline earths. They also serve as excellent adsorbents for steam and vapor and are used as desiccating agents. Another characteristic of dehydrated clays is their high catalytic activity in both organic and inorganic catalytic reactions. Knoté<sup>65</sup> expressed the dehydration of clays as follows:  $(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O})_2 \longrightarrow \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 + 4\text{H}_2\text{O}$ . Mellor and Holdcroft<sup>73</sup> assumed the formation of free alumina, silica, and water. Two general types of clays are known: (1) the 1 : 1 kaolinite-halloysite type and (2) the 2 : 1 pyrophyllite-montmorillonite type. The first group is characterized by a moderate degree of dispersion and a low chemical reactivity expressed in a small base exchange capacity and low electrical conductivity. The second group shows an expanding lattice and high base exchange capacity. The exchangeable cations reside chiefly in the spaces between the layers where they are associated with water molecules (C. E. Marshall: Paper presented at the 14th Colloid Symposium, Minneapolis, Minn., June 10-12, 1937).

Some of the physical properties concerned in the selection of clays as carriers are tensile strength, modulus of rupture and compression. The nature and amount of colloidal constituents in a clay form the basis for the determination of these factors. Table 21 lists these properties for various types of clays.

Table 21. Physical Properties of Clays.

Type	Tensile Strength (lbs. per sq. in.)	Modulus of Rupture (lbs. per sq. in.)	Compression (lbs. per sq. in.)
English china clay.	41	98	228
English ball clay.	210	588	48
American ball clay.	125	380	633
Florida kaolin.	104	239	539
N. C. kaolin.	69	166	349
Georgia kaolin.	147	325	455
Pennsylvania kaolin.	155	508	631
Ohio shale.	136	311	636

It is assumed that the development of the crystalline phase is significant with regard to these physical properties, coarse crystallization giving unfavorable results, while recrystallization gives favorable results (Mellor). In considering the mechanical properties of fine clays, it is necessary to take into account the ease with which lattice units (clays are built as layer lattices) may slide over one another or become separated.

Heat treatment of clays may change their physical characteristics to a considerable extent. Excessive heating (200-400°) of ball and plastic clays may result in a loss in plasticity, an increase in shrinkage, and a decrease in the resistance to compression. Plasticity of clays is a function of particle size and shape.

The physical properties of refractory clays were determined at a temperature of 1350° or above and a pressure of 25 to 40 pounds per square inch (Table 22).

Table 22. Low Resistance to Deformation Used in Testing Refractory Clays.

Physical Property	lbs. per sq. in.
Compression.	2,000–40,000
Modulus of Rupture.	500–6,000
Elasticity.	500,000–7,000,000
Tensile strength.	500–5,000

*Ceramics.*—Ceramics are materials made from (1) white burning clays, Cornish stone and flint (earthen ware), (2) a mixture similar to (1) but containing more fluxes and fired at higher temperature (vitreous ware and ironstone), (3) clays, feldspar and quartz, with or without lime (hard porcelain), (4) bone ash, clay and Cornish stone (ton china), (5) a calcareous marl and glassy frit (soft porcelain), (6) special mixtures, often local clays, glazed with a mixture containing galena (terra-cotta ware), etc. The grain size of the components in all ceramic materials influences their properties greatly. Technical clay from which ceramics are obtained contains non-plastic material, sand, or quartz mixed with colloidal aluminum silicate or with silicic acid and alumina. Sand may cake and be molded by the addition of water. When sand is wet, each sand particle is enveloped by a thin membrane of water which draws the individual grains together; the smaller the grains of sand, the greater the surface tension of the water layer, and the greater the force exerted when sand is molded. While water and oil wet clay and aid in the formation of a plastic mass, other substances, such as ether and mineral oil, do not penetrate into or flow between single clay particles, thereby retarding the formation of a plastic mass. Fine grinding and electrophoresis, with the addition of suitable electrolytes which serve as dispersion agents, convert non-plastic substances, such as sand or quartz, into material suitable for molding. Heat treatment of ceramic materials causes a decrease in the porosity of the mass, but only at higher temperatures, resulting in an increase in the fineness of the quartz, while at lower temperatures the porosity of the mass increases with an increase in the fineness of the quartz. The degree of dispersion and the temperature greatly influence the physical properties of ceramic materials, namely, coefficient of expansion, resistance to changes in temperature, solidity, and transparency. The difference in the behavior of a ceramic material when treated with heat depends upon whether it has been molded wet or pressed dry. A certain dry-pressed clay was 3 per cent porous at 1159°, while the same clay when wet-molded was 3 per cent porous at 1111°.

The colloidal constituency of a clay renders the ceramic mass plastic. Even for very plastic clays the number of colloidal particles (average diameter less than 140 $\mu\mu$ ) scarcely reaches 3 per cent. Ehrenberg and Given,<sup>38</sup> in their chemical analysis of colloidal clays, assumed that the colloidal part of the clay was in the form of an emulsion rather than in a

suspension. Substances such as alkalis, humus and organic compounds present in ceramic materials prevent the partial precipitation of clay; on the other hand, they induce precipitation due to oxidation, hydrolysis and diffusion processes. The removal of these precipitants by washing with water may improve the plasticity of the clay.

*Bentonite*.—Bentonite, a clay-like substance, may also serve as a carrier for catalysts. Deposits of bentonite may be found in various parts of the United States (California, Arizona, Oklahoma, South Dakota, Utah and Wyoming), as well as in Canada. A chemical analysis of bentonite shows that it contains 60 to 65 per cent silicon oxide and 20 to 25 per cent aluminum oxide and ferric oxide. Bentonite from Belle Fourche (South Dakota) has the following composition: silicon oxide, 60.64 per cent; aluminum oxide, 23.26 per cent; ferric oxide, 3.92 per cent; calcium oxide, 0.59 per cent; magnesium oxide, 2.19 per cent, and sodium oxide, 4.33 per cent. Bentonite having a 5 to 10 per cent alkali content is fine-grained, highly adsorbent, with decided colloidal properties, such as plasticity and thixotropy.

For methods of deposition of a catalyst on clay substances, reference may be made to Skita,<sup>99</sup> who describes the deposition of nickel on a clay carrier. The clay was heated in a glass tube to 300° in a stream of hydrogen, boiled with dilute hydrochloric acid to remove the iron and then washed with water until acid-free. After washing, the carrier was reheated until porous; after cooling, melted nickel nitrate previously freed from water of crystallization was deposited on it. The impregnated clay was dried, heated to about 500° either in a reduction tube or in a crucible, and reduced in a stream of hydrogen.

Comp. Internationale pour la Fabrication des Essences de Pétrole<sup>31a</sup> recommends mixing white clay or kaolin with binding materials, such as sawdust or mazut, molding the mixture in short cylindrical form and subjecting it first to a reducing flame and then to an oxidizing flame.

*Alumina, Corundum and Bauxite*.—When siliceous materials cannot be used as carriers in catalytic reactions because they form silicates with the catalyst on heating, thereby suppressing its activity, substances rich in aluminum or magnesium, such as alumina, corundum, and bauxite are substituted.

Alumina is the oxide of aluminum,  $\text{Al}_2\text{O}_3$ , and is the most widely distributed earth. When alumina is prepared artificially, it is a white, tasteless, amorphous powder. The addition of copper to alumina is believed to give it greater strength; the presence of manganese promotes resistance to corrosion; silicon imparts an abrasive quality.

Corundum is native crystallized alumina,  $\text{O}=\text{Al} \begin{array}{c} \diagup \quad \diagdown \\ \text{O} \end{array} \text{Al}=\text{O}$ , or aluminum

oxide occurring in rhombohedral crystals and also in masses and grains. The term "corundum" is applied specifically to non-transparent kinds used as abrasives and is the hardest mineral except the diamond. It has a hardness of 9 and a specific gravity of 3.95 to 4.10.

Bauxite is a ferruginous hydrate of alumina,  $\text{HO} \begin{array}{c} \diagup \text{Al} \diagdown \\ \text{HO} \quad \text{OH} \\ \parallel \\ \text{O} \end{array} \text{OH}$  occurring

in oölitic masses and in earthy form. A typical bauxite is high in alumina and relatively low in silicon, iron, and other impurities. It is composed essentially of 55 to 65 per cent aluminum oxide; 2 to 5 per cent silicon; 1.0 to 2.5 per cent ferric oxide; 1 to 3 per cent titanium dioxide, and 10 to 30 per cent combined water. Bauxite as found in the United States contains 58 per cent alumina and 5 to 6 per cent silica, and is used largely in the preparation of aluminum and alumina and for the lining of furnaces which are exposed to intense heat. About 2 tons of bauxite are required to make 1 ton of alumina and 2 tons of alumina are required to make 1 ton of aluminum.

In catalytic reactions in which alumina may be self-reactive, Alundum, artificially prepared corundum, is substituted. Snelling<sup>100</sup> considered Alundum suitable as a support for copper catalyst in the preparation of formaldehyde from methyl alcohol. The National Aniline and Chemical Company (Paunett)<sup>76</sup> recommends the use of Alundum as a carrier for vanadium pentoxide in the preparation of maleic anhydride. In some cases the activity of nickel as a dehydrogenating agent may be decreased by precipitating the metal on a carrier, such as alumina,<sup>88, 121</sup> the catalyst in this instance resembling palladium and platinum in its action. Zelinsky and Komarewsky<sup>121</sup> prepared nickel catalyst by (1) dissolving 145 grams of nickel in nitric acid and washing the precipitate to remove the excess acid:  $3\text{Ni} + 8\text{HNO}_3 \longrightarrow 3\text{Ni}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO}$ ; (2) treating 175 grams of aluminum nitrate with sodium hydroxide:  $2\text{Al}(\text{NO}_3)_3 + 6\text{NaOH} \longrightarrow 2\text{Al}(\text{OH})_3 + 6\text{NaNO}_3$ ; and (3) combining (1) with (2), saturating the precipitated hydroxide with carbon dioxide, and mixing with 55 grams of pure, dry, unglowed alumina. The precipitate is filtered off, washed with water to remove any excess alkali and nickel nitrate, dried at  $120^\circ$  and reduced at  $300$  to  $330^\circ$ . (The loss of water by glowing alumina is about 48 per cent.) The catalyst supported on alumina is in the form of small black grains and the content of the nickel is about 56 per cent. Fritzweiler and Stuer of the Chemische Fabrik in Rhenania<sup>28</sup> prepared contact substances, such as ferric oxide, on bauxite.

**Salts.**—The salts most frequently used as carriers are magnesium sulfate, calcium carbonate and barium sulfate. While porous supports for catalysts are useful in facilitating reactions in a gaseous phase, there are processes in which the penetration of the catalyst into the interior of the carrier is not advantageous. This fact has been recognized in German Patent 128,554, issued April 2, 1901, in which spraying granular calcined magnesium sulfate with a platinum chloride solution is advocated. Bush and Stöve<sup>26</sup> used calcium carbonate as a carrier for a palladium catalyst. Fifty grams of calcium carbonate precipitated from a hot solution of calcium chloride and sodium carbonate ( $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{NaCl}$ ) were thoroughly washed to remove any excess alkali, the water-suspended precipitate treated with one gram of palladium chloride solution,

gentle heat applied, and the palladium precipitated as a hydroxide on the carbonate. Frequent washing of the catalyst on the carrier should be avoided, because palladium hydroxide passes into solution. Palladium on calcium carbonate may be readily regenerated by treating with acetic acid.

The precipitation of a 5-per cent palladium solution on barium sulfate has been described by Rosenmund.<sup>87</sup> Schmidt<sup>92</sup> suspended 20 parts of hot precipitated barium sulfate in 400 parts of hot water contained in a porcelain dish, to which was added 1.7 parts of palladium chloride solution (corresponding to one part of palladium) in 50 parts of water, and one part 40- to 50-per cent formaldehyde solution made slightly alkaline with sodium hydroxide; the mixture was heated to boiling and the precipitate filtered and washed with hot water until neutral in reaction. The catalyst-carrier obtained was dried over sodium hydroxide in a desiccator, pulverized, and stored in a glass container.<sup>61</sup>

The precipitation of a catalyst on a carrier may also be effected by dipping the substance first into one of two reacting solutions and then into the other, but the resulting precipitate covers the outer surface of each particle, clogs the capillaries, and interferes with diffusion into the interior of the carrier. Catalysts may be plated on carriers such as glass, porcelain, marble, mica, quartz, and metal wires. A colloidal metallic solution may be dried on the surface of the carrier, covering it with a thin layer of the reduced metal; or the catalyst may be prepared in the form of a paste and supported on the carrier. For example, cupric oxide is precipitated from 20 grams of hot neutral copper acetate solution to which has been added an excess of sodium hydroxide solution ( $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O} + 2\text{NaOH} \longrightarrow 2\text{NaC}_2\text{H}_3\text{O}_2 + \text{Cu}(\text{OH})_2 + \text{H}_2\text{O}$ ), the precipitate washed three or four times, dried on a water bath to form a soft paste, which is packed on a copper wire in spiral form and reduced at 280° in a stream of hydrogen until no more water is given off.

An iron-aluminum alloy precipitation on iron metal particles is described by Downs.<sup>35</sup> Bogdanow and Leznow<sup>20</sup> describe a catalyst carrier for the oxidation of toluene to benzaldehyde. Higher oxides of vanadium and molybdenum, either singly or in a mixture, are partially reduced in an acid medium by ferro-chromium alloy and the oxides precipitated by evaporating the solution. For example, to 10 parts of ammonium molybdate dissolved in 15 parts of water and 15 parts of 10-per cent hydrochloric acid solution are added 130 parts of ferro-chromium alloy; the mixture is heated on a water bath, dried, screened till free from dust, and the ferro-chromium alloy together with the precipitated molybdenum oxide heated to red heat; air is blown through the mass at 400–410°. The most desirable working temperatures for this reaction are those ranging between 490 and 510°. Second, to a solution of 7 parts ammonium molybdate and 0.85 part ammonium vanadate in 15 parts of water and 10 parts of 10-per cent hydrochloric acid solution are added 150 parts of iron-chromium alloy (particle size 2–5 mm.); the mixture is stirred, evaporated to dryness and the precipitate slightly glowd. The depth of the catalyst layer is estimated to be 130 mm. Third, to 1.0 part of ammonium molybdate dissolved in a small amount of water containing 1.0 part of hydrochloric acid (sp. gr. 1.19) is

added 0.6 part tin; after reduction, a solution of 10.0 parts of ammonium molybdate is added to the mixture.

From a discussion of methods of deposition of catalysts on single carriers, it is deduced that in general they may be divided into two groups (Table 23).

Table 23. Methods for the Deposition of Catalysts on Carriers.

- I. Surface Deposition:
  - a. Precipitation of the catalyst on a carrier.
  - b. Electroplating " " " " "
  - c. Coating the carrier with a paste.
  - d. Deposition of colloidal metals in which a spreading of the reduced metal in a nascent state takes place.
- II. Internal Deposition:
 

(uniform distribution of the reduced metal of the catalyst throughout the carrier; the internal surface of the carrier is coated).

  - a. Permeating or impregnating porous supports, such as charcoal or gel, with a salt solution.
  - b. Simultaneous precipitation of oxides.

In choosing a carrier, it is essential to know for what type of catalytic reaction it is most suited. It is a well-known fact that many reactions are aided by contact with solid surfaces. Porous contacts are efficient in oxidation, hydrogenation, chlorination, and other processes, as they are able to adsorb oxygen, hydrogen, chlorine, etc., thereby facilitating their transfer to and action with the catalyzed components of the reacting system. Thus the nature and functions of a carrier may be specific not only with respect to the catalyst, but also with respect to the particular type of reaction. While deposition of platinum or palladium on silica gel, kieselguhr and other carriers considerably increases the hydrogenating ability of these catalysts, the hydrogenating action of platinum deposited on charcoal is insignificant. Similarly, barium sulfate or pumice carriers retard the catalytic activity of palladium. The effect is negative also when these catalysts are deposited on carbonaceous substances, such as starch and derivatives of saturated hydrocarbons. The dehydrogenating ability of platinum, when deposited on charcoal, as well as on cellulose, increases to such an extent that the reaction takes place at room temperature.<sup>66, 122</sup>

The type of carrier to be used in a catalytic reaction is also determined by physical conditions (temperature and pressure, duration of the reaction, etc.) under which the reaction is to take place. In some cases it may be important to use fireproof or heat-resisting materials (asbestos) as a carrier; in other instances, for example, when working under high pressure, it may be necessary to emphasize the mechanical resistance factor in the choice of a carrier. In order to withstand pressure, material used as a carrier must be of a certain hardness and have compression strength. Chemical resistance, and especially resistance to poisons, is of particular concern in certain types of catalytic reactions, and in these cases chemical inertness or selective type of adsorption may be involved.

In order to determine the specificity of an individual carrier with respect to the catalyst and the type of catalytic reaction in which it participates, tabulations were made listing the type of reaction, its corresponding

catalyst, and the supporting carrier (Tables 24-43). Also a cross-section showing the individual carriers with reference to a group of catalysts which they support, is presented in Tables 44-50.

Table 24. Carbonaceous Material as a Carrier.

<i>Synthetic Reactions</i>			
Reaction	Catalyst	Carrier	Observer
Synthesis of higher alcohols.	Pd.	Charcoal.	Commercial Solvents Corp.: G.P. 417,926, Cl 120 August 22, 1925.
Preparation of butanol from ethanol: $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_2 = \text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	( $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ ) promoted by Yt (Zr, La).	Bone charcoal.	Dolgow and Wolnow: <i>Zhur. Obschei Khim.</i> , 3 (65) 313-318 (1933).
Synthesis of formic acid from CO (69 p.) and $\text{H}_2\text{O}$ vapor (25 p.); temp. 325-900°; 50% theoretical yield.	Boryl phosphate.	Wood charcoal.	E. I. Du Pont de Nemours & Co. (Vail): U.S.P. 1,895,238, January 24, 1933.
Synthesis of propionic acid.	$\text{CaCl}_2$ or $\text{ZnCl}_2$ .	Active carbon.	E. I. Du Pont de Nemours & Co. (Carpenter): U.S.P. 1,927,767, August 29, 1933.
Synthesis of propionic acid from 72% CO, 3% $\text{C}_2\text{H}_4$ and 25% water vapor; temp., 325° pressure, 700 atm; 75% yield.	$\text{NH}_4\text{Cl}$ , $\text{NH}_4\text{Br}$ or $\text{NH}_4\text{I}$ (1% aqueous solution of $\text{NH}_4\text{Cl}$ in a vapor phase).	Active carbon.	E. I. Du Pont de Nemours & Co. (Larson and Vail): U.S.P. 1,924,765, August 29, 1933.
Synthesis of propionic acid from $\text{C}_2\text{H}_4$ ; temp. 325°; pressure, 700 atm.	Inorganic, volatile acids or halides.	Activated charcoal.	E. I. Du Pont de Nemours & Co.: U.S.P. 1,924,768, August 29, 1933.
Synthesis of trimethyl acetic acid: $(\text{H}_3\text{C})_2\text{CH} \cdot \text{CH}_2\text{OH} + \text{CO} \rightarrow (\text{H}_3\text{C})_2 \cdot \text{COOH}$ temp., 300°; pressure, 700 atm.	Hydrogen halide.	Activated charcoal.	E. I. Du Pont de Nemours & Co. (Larson): U.S.P. 1,995,930, March 26, 1935.
Synthesis of formic acid: $\text{CO} + \text{H}_2\text{O} + \text{NH}_3 \rightarrow \text{H} \cdot \text{COONH}_4$	$\text{CuCl}$ .	Charcoal.	Dubose: <i>Rev. des Prod. Chim.</i> , 27, 433-434 (1924).
Synthesis of methane from CO and $\text{H}_2$ ; temp., 300-400°; pressure, 10-20 atm.	Ni-Mn-Al mixed catalyst.	Activated charcoal or kieselguhr.	Padovani and Franchetti: <i>Atti. Congr. Naz. Chim. pura appl.</i> , 5 (II) 818-828 (1936).
<i>Decomposition Reactions</i>			
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{MnO}_2$ .	Charcoal.	Roiter and Schafran: <i>Zhur. Fiz. Khim.</i> , 4, 461-464 (1933).
Decomposition of $\text{H}_2\text{O}_2$ at 400°.	$\text{Fe}_2\text{O}_3$ or Pt sol.	Activated sugar charcoal (activated at 1000° and less than 2 mm. Hg pressure).	Fowler and Walton: <i>Rec. trav. Chim. Pays-Bas</i> , 54 (4) 476-480, May 12, 1935.
Decomposition of $\text{CaSO}_4$ by $\text{Cl}_2$ at 900-950°; yield 70%.	0.1 g. $\text{NiSO}_4$ .	Charcoal.	Brodnikow and Kree: <i>Doklady Acad. Nauk. S.S.S.R.</i> , 3, 161-166 (1936).
Decomposition of $\text{CH}_3\text{COOH}$ .		Charcoal.	Kultaschew and Rudischewa: <i>J. Russ. phys.-Chem. Soc.</i> , 55, 383-396 (1924).

Table 24 (Continued).

## Oxidation Reactions

Reaction	Catalyst	Carrier	Observer
Oxidation of ethyl alcohol: $\text{CH}_3\text{CH}_2\text{OH} + (\text{O}_2) \rightarrow$ $\text{CH}_3\text{C}=\text{H}=\text{O} + \text{H}_2\text{O}$	Ag.	Charcoal, brown coal, or pitch.	Demestedt and Hassler: G.P. 203,348 (1907). Goldschmidt: Brit. P. 290,523 (1927); U.S.P. 1,666,447 (1928). Holzverkohlung Ind. A.-G.: Brit. P. 294,037 (1927).
Conversion of arsenous oxide to arsenic pentoxide; increase in yield from 42% to 98%.	CuO.	Activated charcoal.	Adadurow and Dzisko: <i>Z. phys. Chem. (Russ.)</i> , 3, 489-495 (1932).
Oxidation of acetylene at 400-410°: (1) $\text{C}_2\text{H}_2 + \text{H}_2\text{O} \rightarrow$ $\text{CH} \cdot \text{CHO}$ (2) $2\text{C}_2\text{H}_2 + 3\text{H}_2\text{O} \rightarrow$ $\text{CH}_3\text{COCH}_3 + \text{CO}_2$ (3) $\text{C}_2\text{H}_2 +$ $2\text{CH}_3 \cdot \text{COOH} \rightarrow$ $\text{CH}_3\text{CH}(\text{OCOCH}_3)_2$	Mixture of 35 g. Zn acetate and 10 g. Mn acetate.	Porous charcoal, 200 g.	Deutsche Gold u. Silber Scheideanstalt (Roesler, Walter and Schultze): G.P. 577,705, Kl 12o, June 3, 1933.
Oxidation of acetylene to acetone.	Mixture of Zn or Cd basic cmpds. as well as mixture of alkalies or alkali earths.	Wood charcoal (highly active).	Deutsche Gold u. Silber Scheideanstalt (Roesler and Walter): G.P. 584,517, Kl 12o, September 21, 1933.
Oxidation of acetic acid to acetone.	Cu, Al, V, 2A-steel.	Charcoal or ceramic mass.	Deutsche Gold u. Silber Scheideanstalt (Roesler, Walter and Schultze): G.P. 581,047, Kl 12o, July 20, 1933.
Oxidation of acetic acid to acetone.	CaO, Fe, ZnO, Ba(OH) <sub>2</sub> .	Activated charcoal (from carbon-containing substances treated with ZnCl <sub>2</sub> and partially oxidized by air or water vapor).	Deutsche Gold u. Silber Scheideanstalt (Roesler): G.P. 627,195, Kl 12o, March 10, 1936.

## Reduction Reactions

Reduction of oxygen-containing organic compounds.	Fe, Cr, or Ni.	Charcoal.	Handelsondernaming (Feynald): G.P. 434,211, Kl 12o, September 21, 1926.
Reduction of CO <sub>2</sub> : $\text{CO}_2 + \text{C} = 2\text{CO}$ ; temp. 150-200°.	Na <sub>2</sub> CO <sub>3</sub> .	Wood charcoal.	Edenholm and Widell: 4A, 26-39, April 1, 1934.
Reduction of ketones (propiophenone in alcoholic solution).	Pd.	Bone charcoal.	Hartung and Crossley: <i>J. Am. Chem. Soc.</i> , 56, 158-169 (1934).

## Hydration and Dehydration Reactions

Hydration of ethylene hydrocarbons at 150°; yield of alcohol, 15-20%.	CuO + WO <sub>3</sub> .	Activated charcoal.	N. V. deBataafsche Petroleum Maatschappij: Brit. P. 335,551.
Hydration of ethylene in the preparation of ethyl alcohol at 150°; yield, 2%.	70% H <sub>2</sub> SO <sub>4</sub> + Ag <sub>2</sub> SO <sub>4</sub> (fatigue of the catalyst is a disadvantage).	Activated charcoal.	Balandin and Neswinsky: <i>Sci. Communication (Moscow Univ.)</i> , 2, 233-235 (1934).
Dehydration of ethyl alcohol.	Al <sub>2</sub> O <sub>3</sub> .	Birchwood charcoal.	Adadurow and Kraini: <i>Zhur. Fiz. Khim.</i> , 5, 136-144 (1934).



Table 24 (Continued).  
*Hydrogenation and Dehydrogenation Reactions*

Reaction	Catalyst	Carrier	Observer
Hydrogenation of fats.	Ni.	Charcoal.	Ellis: U.S.P. 1,060,673 (1912). Dewar: Brit. P. 15,668 (1914).
Hydrogenation of oils or other organic compounds.	Ni carbonyl.	Dried oak wood.	Lessing: E.P. 152,740, November 18, 1920.
Hydrogenation of ethers in the preparation of alcohols.	Pd.	Charcoal.	Commercial Solvents Corp.: G.P. 417,926, Kl 120, August 22, 1925.
Hydrogenation of fatty acids (oils).	Ni.	Activated coal, kieselguhr, or pumice.	Uno and Saida: <i>J. Soc. Chem. Ind. (Japan)</i> , 30, 107B (1927).
Hydrogenation of fatty oils.	Ni.	Activated charcoal.	Jozsa: <i>Z. ang. Chem.</i> , 41, 767-771 (1927).
Hydrogenation of ethylene.	Ni.	Activated wood, charcoal.	Schuster: <i>Chem. Age</i> , 26, 46, January 16, 1932.
Hydrogenation of olefins at 150-250°.	ThO <sub>2</sub> or Pt, Au, Cu, W or their compounds.	Charcoal.	Dreyfus: E.P. 389,136, April 6, 1933.
Joint hydrogenation of cresols and naphthalene.	NH <sub>3</sub> molybdate.	Charcoal.	Klukwin, Polozow and Lobuss: <i>Khim. Trerdogo Topliva</i> , 5, 357-372 (1934).
Hydrogenation of substituted W nitrostyrenes.	Pd.	Bone charcoal.	Reichert and Koch: <i>Ber.</i> , 273, 265-274 (1935).
Hydrogenation of simple homologs of cyclopentane.	Pt.	Charcoal (activated at 305-315°).	Zelinsky and Kasansky: <i>Ber.</i> , 68, 1869-1872, September 11, 1935.
Preparation of a gas free from CO or CO-containing combustible gases; two stages in the process: (1) oxidation. (2) hydrogenation.	(1) Cr <sub>2</sub> O <sub>3</sub> containing Fe. (2) Ni + ThO <sub>2</sub> .	Activated charcoal. Activated charcoal.	Kemmer: G.P. 617,565, Kl 26a, August 21, 1935.
Hydrogenation of fuels.	Finely dispersed colloidal MoS <sub>2</sub> .	Activated charcoal (freed to the greater part of ash by an acid treatment).	N. V. deBataafsche Petroleum Maatschappij: F.P. 745,074, May 2, 1933.
Hydrogenation of carbon-containing compounds.	MoS <sub>2</sub> treated with HCl (300-400°); MoCl <sub>5</sub> liberated thereby led upon SiO <sub>2</sub> gel adsorbed on it and treated with CO <sub>2</sub> and a mixture of H <sub>2</sub> S and H <sub>2</sub> substituted, cooled.	Activated charcoal or bauxite.	N. V. deBataafsche Petroleum Maatschappij: F.P. 754,664, November 10, 1933.
Hydrogenation of solid carbon-containing substances, such as brown coal or bituminous coal.	Mo acid in CH <sub>3</sub> OH (0.02% Mo acid serves for impregnation).	Reacting substance itself serves as a carrier for the catalyst.	International Hydrogenation Patents Co., Ltd. (I. G. Farbenindustrie A.-G.): E.P. 427,275, May 16, 1935; F.P. 778,674, March 22, 1935.
Hydrogenation of solid carbon-containing substances at 400° under 100 atm. H <sub>2</sub> pressure.	Na aluminate.	Charcoal powder admixed with anthracene oil.	Compagnie des Mines de Vicoigne (Noeu and Drocourt): E.P. 447,930, June 25, 1936.

Table 24 (Continued).

Reaction	Catalyst	Carrier	Observer
Pressure hydrogenation of fuels.	Colloidal Re or its compounds in a colloidal state, <i>e.g.</i> , Resulfide (ppt. with $H_2S$ and acidified with $H_2SO_4$ sol of $R \cdot ReO_4$ ).	Activated charcoal.	N. V. deBataafsche Petroleum Maatschappij: E.P. 358,180, October 29, 1931.
Pressure hydrogenation of baked coal.	Al molybdate solution impregnated.	Charcoal.	I. G. Farbenindustrie A.-G.: F.P. 736,863, November 30, 1932.
Pressure hydrogenation of fuels at 425° and 200 atm. pressure.	Halide compounds of Mo, U, V, or I compounds of Ag, Cu, Ni, Sn, Mn, Ni and Co or their mixtures.	Activated charcoal $SiO_2$ gel. or pumice.	I. G. Farbenindustrie A.-G.: F.P. 747,459, June 17, 1933.
High pressure and temperature hydrogenation of coal at 460° for 3 hours; 93% of coal is converted into liquid hydrocarbons.	Ammonium molybdate solution; 0.1% of $MoO_3$ .	Charcoal.	I. G. Farbenindustrie A.-G.: G.P. 570,951, Kl 120, February 22, 1933, F.P. 738,995, January 4, 1933.
Pressure hydrogenation of solid carbon-containing substances, such as brown coal, pitch, "torbanit" wood, and especially bituminous coal at 380-470° and 200-300 atm. hydrogen.	Sn oxalate or Mo acid.	Reacting substance itself a carrier.	Imperial Chemical Industries, Ltd.: F.P. 775,721, January 8, 1935; E.P. 425,679, April 18, 1935.
Hydrogenation of carbonaceous materials.	Pd or its cmpds. (oxides, sulfides, chromates).	Charcoal.	International Hydrogenation Patents Co., Ltd.: F.P. 793,799, January 31, 1936.
Pressure hydrogenation of naphthalene and benzene.	Ammonium molybdate solution and $H_2S$ or ammonium vanadate.	Activated charcoal.	International Hydrogenation Patents Co., Ltd.: F.P. 728,287, July 4, 1932; E.P. 379,587, September 22, 1932.
Destructive hydrogenation of mineral or tar oils under pressure.		Charcoal paste.	Zotos: E.P. 386,993, February 23, 1932.
Destructive hydrogenation of fuels.	$MoS_2$ ; ammonium molybdate precipitated with $H_2S$ and the precipitate treated with $H_2$ under 300 atm.	Activated charcoal.	N. V. deBataafsche Petroleum Maatschappij: F.P. 745,468, May 11, 1933.
Destructive hydrogenation of solid carbon-containing substances such as bituminous coal at 410-480°.	0.2% $PbCl_2$ admixed with oil, 1:1; halides of P, S, Se, As and Sb.	Bituminous coal itself a carrier.	International Hydrogenation Patents Co., Ltd.: F.P. 793,464, January 25, 1936.
Dehydrogenation of mineral oils, benzene, naphthenes at 200-300° under elevated or diminished pressure.	Ammonium molybdate or $Pb(NO_3)_2$ and $H_3PO_4$ (treated with $H_2S$ at 300°). Ammonium tungstate, $Co(NO_3)_2$ and $Sb_2O_3$ (treated with $H_2S$ at 350°). Ammonium vanadate $Co(NO_3)_2$ and $H_3PO_4$ (mixture brought on carrier treated with $H_2$ and $CS_2$ at 350°).	Activated charcoal.	I. G. Farbenindustrie A.-G.: E.P. 333,995, September 18, 1930.
Dehydrogenation of benzene, coal, hydrogenation products or hydroaromatics, such as cyclohexane, at 430°.	$FeCl_3$ .	Charcoal.	I. G. Farbenindustrie A.-G.: F.P. 448,442, July 4, 1933.

Table 24 (Continued).

Reaction	Catalyst	Carrier	Observer
Dehydrogenation of pressure hydrogenation products.	Dehydrogenation catalysts or compounds of the 6th group, e.g., Mo oxides or $\text{ZnO}$ , $\text{Al}_2\text{O}_3$ , likewise mixed with $\text{CdS}$ , $\text{ZnS}$ , or $\text{Cr}_2\text{O}_3$ .	Activated charcoal.	I. G. Farbenindustrie A.-G. (Mittasch and Langheinrich): U.S.P. 1,913,940 and 1,913,941, June 13, 1933.
Dehydrogenation of organic compounds.	Halogen cmpds. of Cu, Ag, Zn, Cd, Pb, Sn, Ti, Si, V, Bi, Mo, W, U, Mn, Re, Ni, Fe, or Co.	Activated charcoal.	I. G. Farbenindustrie A.-G.: F.P. 748,442, July 4, 1933.
Dehydrogenation of 43% crude oil with a high percentage of aromatic hydrocarbons at $160^\circ$ .	30% Pt.	Activated charcoal.	Zelinsky and Schuilkin: <i>Khim. Zhur. Ser. A</i> , 4 (66) 901-905 (1934).
Dehydrogenation of methyl cyclohexane to toluene at $290-300^\circ$ .	Pt.	Activated charcoal (30 g., active coal stirred with $\text{H}_2\text{PtCl}_6$ solution containing 5.2 g. Pt).	Packendorff and Leder-Packendorff: <i>Ber.</i> , 67, 1388-1391, August 8, 1934; refer also to Zelinsky and Borisow C. 1924, I 1142.
Dehydrogenation of a fraction of Surachan benzene (Baku) rich in hydroaromatics.	Pt.	Activated charcoal.	Zelinsky and Schuilkin: <i>Izvestiya Akad. Nauk S.S.S.R.</i> , (7), 229-237 (1935).

## Desulfurization Reactions

Desulfurization of substances containing carbon, such as petroleum asphalt.	$\text{MoO}_3$ (ppt.).	Activated charcoal.	N. V. deBataafsche Petroleum Maatschappij: Jugoslavia P. 9,950, May 1, 1931.
Desulfurization of a crude oil fraction at $440-480^\circ$ and under 85-100 atm. $\text{H}_2$ .	$\text{MoO}_3(\text{NH}_4)_2\text{MoS}_4$ ; colloidal Mo and Cu chromite.	Activated charcoal.	Pertierra: <i>Anales soc. espan. fis. quim.</i> , 31, 289-310, July 15, 1933.

## Chlorination Reactions

$\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$ $\text{C}_2\text{H}_2 + 2\text{Cl}_2 \rightarrow \text{C}_2\text{H}_2\text{Cl}_4$	$\text{SbCl}_5$ .	Activated charcoal.	Askenasy and Mugdan: G.P. 154,657 (1903).
Preparation of dichloroethylene, $\text{COOCH} : \text{CHCl}$ by reaction of $\text{C}_2\text{H}_2$ with $\text{Cl}_2\text{CCH}_2\text{Cl}$ or $\text{Cl}_2\text{HCCHCl}_2$ at $350^\circ$ .	Ni.	Activated charcoal.	Chemische Fabrik Heyden A.-G. (Wiegand): G.P. 566,034, April 2, 1931.
Preparation of tertiary alkyl monochlorides from gaseous or liquid olefins.	20% $\text{SnCl}_4$ (impregnated at $150^\circ$ ).	Activated charcoal.	Prins: <i>Rec. trav. Chim. Pays-Bas</i> , 51, 1065-1080 (1932).
Preparation of ethyl halogenides from $\text{C}_2\text{H}_4$ and hydrogen halide.	$\text{ZnCl}_2$ (in active form); activators: halides of Li, Mg, Ca, Cu, Sn.	Wood charcoal or active $\text{SiO}_2$ .	I. G. Farbenindustrie A.-G.: F.P. 793,744, January 30, 1936.

## Miscellaneous Reactions

Preparation of hydrocarbons.	Metals.	Charcoal.	Badische Anilin u. Soda Fabrik: G.P. 295,203, Kl 12o Gr 1, November 8, 1916.
Preparation of catalytic material under diminished pressure.	Volatile chlorides of Al and $\text{NH}_3$ ; $\text{ZnCl}_2$ , excluded.	Briquettes of charcoal.	Badische Anilin u. Soda Fabrik: G.P. 338,852, Kl 12i, July 4, 1921.
Gas reactions.	$\text{H}_3\text{PO}_4$ .	Activated charcoal (treated with $\text{H}_3\text{PO}_4$ ).	Meister Lucius Farbwerte: F.P. 554,076, June 5, 1923.

Table 24 (Continued).

Reaction	Catalyst	Carrier	Observer
Gas reactions.		Activated charcoal	I. G. Farbenindustrie A.-G.: E.P. 262,475, February 2, 1927.
Esterification of acetic acid (from acetic acid and alcohol).	TiO <sub>2</sub> , ThO <sub>2</sub> .	Activated charcoal.	I. G. Farbenindustrie A.-G.: G.P. 434,279, 1924.
Cellulose solutions.	WO <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> , MoO <sub>3</sub> .	Wood charcoal, coke.	Classen: E.P. 261,494, December 16, 1926.
Catalytic processes.	Metals, metal oxides, or metallic salts.	Graphite, charcoal, coke, soot.	E. E. Berger: F.P. 524,453, September 3, 1921.

Table 25. Silica Gel as a Carrier.

Reaction	Catalyst	Carrier	Observer
Synthesis of water: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$	Metal.	Silica gel.	Sweeringen and Reyerson: <i>J. phys. Chem.</i> , 32, 113-120, 192-201 (1927).
Synthesis of NH <sub>3</sub> .	Ni(NO <sub>2</sub> ) <sub>2</sub> + Fe(NO <sub>2</sub> ) <sub>2</sub> + Al(NO <sub>3</sub> ) <sub>3</sub> or 10N K <sub>2</sub> CO <sub>3</sub> as impregnating solution.	Si(OH) <sub>4</sub> gel.	Marconi: Ital. P. 276,011, January 26, 1929.
Preparation of HCN.	Single metals or their mixtures; Pt and Pd or Pt and Rh; chlorides of the metal compounds placed on carrier and decomposed in a stream of O <sub>2</sub> , N <sub>2</sub> at 1100-1400°.	SiO <sub>2</sub> .	E. I. Du Pont de Nemours & Co., Inc.: F.P. 795,092, March 3, 1936.
Thermal decomposition of Na <sub>2</sub> SO <sub>4</sub> .	CeO <sub>2</sub> , TiO <sub>2</sub> , Fe <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> or kaolin.	Fialkow and Schargorodski: <i>Ukrain. Akad. Nauk, Zapiski Inst. Khim.</i> , 2, 269-283 (1935).
Oxidation of SO <sub>2</sub> to SO <sub>3</sub> .		Gel from sodium silicate, aluminate, titanate, tungstate, or from metal salts, such as FeCl <sub>3</sub> , AlCl <sub>3</sub> , CaCl <sub>2</sub> + free HCl acid.	Patrick: E.P. 159,508, March 24, 1921.
Oxidation of SO <sub>2</sub> : $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	Pt.	Silicic acid gel.	Holmes, Ramsay and Elder: <i>Ind. Eng. Chem.</i> , 21, 850-853 (1929).
Oxidation of SO <sub>2</sub> : $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$	Colloidal Pt.	Silica gel (higher activity for colloidal Pt brought upon ready gel).	Charmadarian and Dachnjuk: <i>Ukrain. Khim. Zhur.</i> , 8, Part 2, 36-43 (1933).
Oxidation of SO <sub>2</sub> to SO <sub>3</sub> .	NH <sub>4</sub> VO <sub>3</sub> ; KVO <sub>3</sub> ; (VO) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> .	Si(OH) <sub>4</sub> (10 to 20 p. SiO <sub>2</sub> to 1 p. V); Si(OH) <sub>4</sub> ppt. from alkali solution so that final solution is slightly alkaline or neutral to congo red; ppt. mixed to a paste with V compound and K <sub>2</sub> SO <sub>4</sub> added; V:K = 1:2½ (3½).	Calco Chemical Co. Inc.: U.S.P. 2,027,316, January 7, 1936.
Oxidation of SO <sub>2</sub> .	KVO <sub>3</sub> .	Silica gel; increase in porosity from 20 to 87% increases the yield from 30 to 97%.	Tschufarow, Tatijewskaja and Kulpina: <i>Zhur. Fis. Khim.</i> , 6, 152-156 (1935).
Manufacture of H <sub>2</sub> SO <sub>4</sub> .	Pt (0.01-0.5%).	SiO <sub>2</sub> (very dense gel).	American Platinum Works: F.P. 803,746, October 7, 1936.

Table 25 (Continued).

Reaction	Catalyst	Carrier	Observer
Oxidation of acetaldehyde to acetone.	19% $\text{Al}_2\text{O}_3$ ; 8.8% Ni tartrate.	Silica gel (dilute $\text{NaNO}_3$ solution is added to purified silica xerogel; yield of acetic acid increases).	Ackermann and Burton: <i>Chem. Age</i> , 31, 169-170 (1934).
Preparation of alcohol from olefins at 125-130° temp. and 25-900 atm. pressure.	Volatile halides $\text{HCl}$ , $\text{HI}$ , $\text{HBr}$ or $\text{CH}_3\text{Cl}$ , $\text{CCl}_4$ , $\text{NH}_4\text{Cl}$ .	Silica gel, pumice, or coke.	E. I. Du Pont de Nemours and Co.: U.S.P. 2,014,740, September 17, 1935.
Reduction of the primary amines of the benzene series.	$\text{Cu}$ , $\text{Ag}$ , $\text{Au}$ .	Silica gel or $\text{Al}_2\text{O}_3$ gel.	I. G. Farbenindustrie A.-G.: E.P. 295,824, September 13, 1928; E.P. 297,212, October 11, 1928.
Hydrogenation of $\text{C}_2\text{H}_2$ to $\text{C}_2\text{H}_4$ .	$\text{Pt}$ or $\text{Cu}$ .	Silica gel.	
Hydrogenation of $\text{C}_2\text{H}_2$ to $\text{C}_2\text{H}_4$ .	$\text{Pd}$ .	Silica gel.	
Hydrogenation of oils (camphor oils).	Metal layer.	Silica gel.	Morris and Reyerson: <i>J. phys. Chem.</i> , 31, 1332-1337 (1926).
Hydrogenation of naphthalene at 325° for 3 hours at 100 atm. $\text{H}_2$ .	20% $\text{NiO}$ .	Silica gel or kaolin; used 27 times more than all other carriers.	Brochet and Schmitz: U.S.P. 1,896,282, February 7, 1933.
Pressure hydrogenation of fuels at 425° and 200 atm.	Halide cmpds. of $\text{Mo}$ , $\text{U}$ , $\text{V}$ , or $\text{I}$ cmpds. of $\text{Ag}$ , $\text{Cu}$ , $\text{Ti}$ , $\text{Sn}$ , $\text{Mn}$ , $\text{Ni}$ and $\text{Co}$ .	Silicic acid gel or active pumice.	I. G. Farbenindustrie A.-G.: F.P. 747,459, June 17, 1933.
Destructive hydrogenation of tars.	$(\text{NH}_4)_2\text{MoO}_4$ solution.	Glowed, grainy aluminum gel.	King and Cawley: <i>Dept. Sci. and Res. Fuel, Res. Tech. Paper No.</i> 41, 17 p. (1936).
The addition of $\text{HCl}$ to $\text{C}_2\text{H}_2$ .	$\text{ZnCl}_2$ .	Silica gel.	Wibaut and van Dalfsen: <i>Rec. trav. Chim. Pays-Bas</i> , 51 (4) 13, 636-640, June 15, 1932.
Ethyl halogenides prepared from $\text{C}_2\text{H}_4$ and hydrogen halide.	$\text{ZnCl}_2$ ; activators: halides of $\text{Li}$ , $\text{Mg}$ , $\text{Ca}$ , $\text{Cu}$ , $\text{Sn}$ .	Active $\text{SiO}_2$ .	I. G. Farbenindustrie A.-G.: F.P. 793,744, January 30, 1936.
Preparation of aliphatic amines from alcohols and ammonia.	$\text{WO}_3$ , $\text{TiO}_2$ .	Silica gel or $\text{Al}_2\text{O}_3$ or $\text{Cr}_2\text{O}_3$ gels in conc. of about 20%.	E. I. Du Pont de Nemours & Co.: E.P. 384,714, January 5, 1933.
Conversion of gases or vapors.	$\text{ThO}_2$ and $\text{ZnO}$ finely dispersed.	Silica gel.	I. G. Farbenindustrie A.-G. (Rötger and Stöweker): U.S.P. 1,828,380 (1930); G.P. 509,582, Cl 12g October 10, 1930.
Hydrolysis of organic halides.	$\text{Cu}$ .	Highly porous silica gel.	Jenkins and Norris: U.S.P. 1,884,710, October 15, 1932.
Polymerization of gaseous hydrocarbons ( $\text{C}_2\text{H}_4$ , $\text{C}_3\text{H}_6$ ) into liquid hydrocarbons at 260-540° and 40-120 atm. pressure.	$\text{AlCl}_3$ , $\text{AlBr}_3$ metal halides, $\text{Pd-Pt}$ sponge, finely divided alloys; metals of the 8th gr.	Silica gel.	Pure Oil Co.: F.P. 680,038, April 24, 1930.
Polymerization of propylene at 350°.	$\text{Al}_2\text{O}_3$ (adsorbed on $\text{SiO}_2$ ).	Porous $\text{SiO}_2$ .	Gayer: <i>Ind. Eng. Chem.</i> , 25, 1122-1127 (1933).
Polymerization of isobutene.	$\text{Al}_2\text{O}_3$ .	Silica gel.	Waterman, Leendertze and deKok: <i>Rec. trav. Chim. Pays-Bas</i> , 53 (4) 15, 1151-1158, December 15, 1934.

Table 25 (Continued).

Reaction	Catalyst	Carrier	Observer
Joint dehydration of ammonia and methyl, <i>n</i> -propyl and <i>n</i> -butyl alcohols.	Blue tungsten oxide or ThO <sub>2</sub> .	Silica gel (prepared at 465°).	Brown and Reid: <i>J. phys. Chem.</i> , <b>28</b> , 1067 (1924).
Dehydration of ammonia and ethyl alcohol.	Thorium.	Silica gel (also alumina).	Briner and Gemdillon: <i>Helv. Chim. Acta</i> , <b>14</b> , 1283 (1931).
Dehydration of formic acid at 280–330°.	P <sub>2</sub> O <sub>5</sub> , TiO <sub>2</sub> +AlPO <sub>4</sub> (activity, not lasting).	Silica gel.	Graeber and Cryder: <i>Ind. Eng. Chem.</i> , <b>27</b> , 825–831 (1935).
Catalytic reactions.	Pd.	Silicic acid.	Berl and Urban: <i>Z. angew. Chem.</i> , <b>36</b> , 57 (1923).
Catalytic reactions.	Catalytic active material.	Porous silicic acid product occurring in Mississippi Valley under the name of tripoli, opalite, carrara silicic acid and geyserite; this has a higher hardness than kieselguhr; prepared in the form of round grains in a rotating drum.	Monsanto Chemical Co. (J. A. Bertsch): U.S.P., 1,933,091, October 31, 1933.

Table 26. Silicates as Carriers.

Reaction	Catalyst	Carrier	Observer
Oxidation of NH <sub>3</sub> to HNO <sub>3</sub> or SO <sub>2</sub> to SO <sub>3</sub> ; Synthesis of NH <sub>3</sub> from N <sub>2</sub> and H <sub>2</sub> .	Ni. Pt, Os.	Silica carbide.	Weintraub: G.P. 354,212, Kl 12g, June 1, 1922; F.P. 532,343, February 1, 1922.
Oxidation of NH <sub>3</sub> .	Alkali.	Cr silicate, V or B silicate.	G.P. 298,981, Kl 12i, June 16, 1926.
Oxidation of NH <sub>3</sub> .	HCl-Co.	W silicates.	E.P. 309,583 (1929).
Oxidation of NH <sub>3</sub> .	Mounted wire spiral of Cr steel or Pt metal or Pt-Rh.	"Celite" sticks (1000–1500°).	Bayerische Stickstoffwerke A.-G.: F.P. 976,205, January 21, 1935.
Manufacture of H <sub>2</sub> SO <sub>4</sub> .	Pt.	Amorphous silicon oxide or silicates strongly acidified.	Verein f. Chemische u. Metallische Produktion: Aust. P. 123,811, July 25, 1931.
Catalytic processes.	A metallic salt solution or in a mixture with other base exchanging substances.	Cr silicate (or other resistant silicates).	Permutite A.-G.: G.P. 365,366, Kl 12g, March 31, 1922.
Catalytic cracking reactions.	Al(OH) <sub>3</sub> (from Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ppt. by NaOH).	Activated Al silicate plus 30% plastic silicate such as alumina.	Comp. Intern. pour la Fabrik des Essence de Petroles: E.P. 324,541, February 20, 1930.
Reduction of organic compounds.	Ni acetate ppt. at low or moderate temperature.	Siloxen (oxydisilin).	G.P. 540,327, Kl 12o, December 18, 1931; add to G.P. 539,177, Kl 12o, November 23, 1931.
Decomposition of hydrocarbons with water vapor, CO <sub>2</sub> , O <sub>2</sub> , or air in H <sub>2</sub> -CO or H <sub>2</sub> -CO-N <sub>2</sub> mixtures.	Metals of the Fe group.	Artificial Al silicate (or unburned natural Al compd., especially kaolin).	I. G. Farbenindustrie A.-G. (Wietzel) (Hennicke): G.P. 554,551, Kl 12i, July 11, 1932.

Table 27. Glass as a Carrier.

Reaction	Catalyst	Carrier	Observer
Decomposition of $\text{H}_2\text{O}_2$ in $\text{NH}_3$ sol.	$\text{CuSO}_4$ (1.54 milli molar sol).	Glass wool.	Quartaroli: <i>Gazz. Chim. Ital.</i> , 61, 466-478 (1931).
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ .	Thin layers of Pt and $\text{V}_2\text{O}_5$ .	Glass.	Dankow, Joffe, Kotschekow and Perewessenzew: <i>Khim. Zhur. S.S.S.R.</i> , 4, 334-342 (1933).
Oxidation of: $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ at $450^\circ$ ; yield, 97-98%.	Mn salts.	Water-glass solution.	Charnadarian and Brodowitsch: <i>Ukrain. Chem. J.</i> , 8, Part 2, 58-65 (1933).
Oxidation of benzene, phenol and furfural to maleic acid.	Oxides of Fe, Co, Ni, Cu, Al, or $\text{V}_2\text{O}_5$ .	Water-glass or non-exchanging base silicate.	Selden Co.: U.S.P. 1,811,363, March 29, 1932.
Hydrogenation of crotonic aldehyde to butyl aldehyde.	Cu.	Water-glass.	Badische Anilin u. Soda Fabrik: G.P. 362,537 (1921).
Hydrogenation of oils with simultaneous bleaching at $150-160^\circ$ .	Ni salt solution + Mg or Al salt.	Water-glass.	Granichstdten and Sittig: Aust. P. 85,954, October 25, 1921; E.P. 147,578, November 10, 1921.
Hydrogenation and dehydrogenation of hydrocarbons: phenol to cyclohexanol at $100-120^\circ$ without the formation of side products; nitrobenzene to aniline; hydrogenation of oils.	$\text{NiCO}_3$ or Cu mixture of Ni and Al compounds.	Water-glass + pumice paste; without water-glass, no satisfactory results.	Badische Anilin u. Soda Fabrik: G.P. 352,439, Cl 12a, May 3, 1922; add to G.P. 307,580.

Table 28. Quartz as a Carrier.

Reaction	Catalyst	Carrier	Observer
Oxidation of $\text{NH}_3$ .	Pt.	Quartz.	Imperial Chemical Ind. Ltd. (Smyth): E.P. 346,800, May 14, 1931.
Oxidation of CO.	$\text{CuO}$ ppt.	Quartz or asbestos.	
Conversion of $\text{CH}_4$ to $\text{H} \cdot \text{CHO}$ .	Mixture of oxides: $\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ .	Quartz or pumice or asbestos.	Bakelite Co.: G.P. 411,215.
Pressure hydrogenation of coal or oil suspensions of coal.	Co, Ni, Cu, $\text{Ce}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$ .	Monazite and sand.	Shering and Kahlbaum A.-G.: F.P. 739,770, July 7, 1932.
Oxidation of benzene, phenol, furfural; (also for purification of anthracene, phenanthrene).	V salt solution; (pieces of alumina or $\text{Al}_2\text{O}_3 \cdot \text{ZnO}$ may be added).	Quartz or glass pieces boiled 1-2 hrs. in NaOH or KOH.	American Cyanamid & Chemical Corporation (Jaeger): U.S.P. 2,035,606, March 31, 1936.
Catalytic reactions.		Threads of quartz as well as quartz wool.	Heracus G.m.b.H.: E.P. 490,118, Sept. 8 (1938).

Table 29. Zeolites as Carriers.

Reaction	Catalyst	Carrier	Observer
Oxidation of $\text{NH}_3$ : (1) $\text{NH}_3 + 2\text{O}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O}$ (2) $4\text{NH}_3 + 5\text{O}_2 \rightleftharpoons 4\text{NO} + 6\text{H}_2\text{O}$	Alkali or alkali earth compounds.	Polyzeolites.	G.P. 298,981, Kl 12i, June 16, 1926; E.P. 309,582, June 6, 1929.
Oxidation of $\text{SO}_2$ : $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	One or more metals or their salts.	Many component zeolites prepared from their silicates.	Selden Co.: E.P. 290,316, June 14, 1928.
Oxidation of $\text{SO}_2$ : $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	Catalyst.	Double zeolite.	Selden Co.: E.P. 296,048, October 17, 1928.
Oxidation of $\text{SO}_2$ : $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	$\text{V}_2\text{O}_5$ , $\text{MoO}_3$ , $\text{Cr}_2\text{O}_3$ , $\text{WO}_3$ , $\text{Mn}_2\text{O}_3$ , $\text{Mn}_2\text{O}_7$ .	Zeolites.	Selden Co.: U.S.P. 1,657,753, January 31, 1928.

Table 29 (Continued).

Reaction	Catalyst	Carrier	Observer
Oxidation of organic compounds in the gaseous state.	V, Mo, Ta, W, Cr, U, Mn, Bi, Fe, Co, Ni, Cu, Ag oxides alone or in mixtures.	Zeolites (double Al silicate); natural zeolites, naphthelite, lenite or feldspar.	Selden Co.: U.S.P. 1,694,122, December 4, 1928.
Oxidation of naphthalene to phthalic anhydride.	V.	Artificial zeolites, <i>e.g.</i> , 42 p. $K_2SiO_3$ , 70 p. zeolite, 18 p. $V_2O_5$ mixed and dissolved in conc. KOH, then mixed with 5 p. $Al_2O_3$ in KOH heated to $60^\circ$ + 10% $H_2SO_4$ which is added until viscous, filtered, dried at $100^\circ$ and pulverized.	Selden Co.: U.S.P. 1,515,299, and 1,599,228.
Oxidation of naphthalene.	Catalysts.	Zeolites.	Selden Co.: U.S.P. 1,692,126, November 20, 1928.
Oxidation of anthracene (vapors) to anthraquinone by air at $400^\circ$ .	K vanadate and Cu or Ni compounds, the basic radical of which is able to enter into a non-exchangeable nucleus of the zeolite.	At least one zeolite, <i>i.e.</i> , reaction product of one silicate such as Na silicate.	Selden Co. (Jaeger): U.S.P. 1,886,023, January 11, 1932.
Hydrogenation of organic compounds.	Pt.	Natural zeolites.	Schneider and Morawitz: U.S.P. 1,215,396, February 13, 1917.
Catalytic reduction and oxidation.	Platinum chloride (potassium osmate or potassium ruthenate).	Zeolites (no direct base exchange).	Badische Anilin u. Soda Fabrik: G.P. 305,001, Cl 12g, November 1, 1920.
Synthesis of $NH_3$ from $N_2$ and $H_2$ .	(1) $NH_3$ molybdate. (2) W chloride.	(1) $NH_3$ zeolite. (2) Na zeolite.	
Reduction of carbonyl compounds (stepwise) at $300$ – $370^\circ$ temp. and $80$ – $150$ atm. pressure.	Catalyst base exchanger; the same as the carrier.	Zeolite (a type of Al silicate or a double silicate; itself serves as a catalyst).	Selden Co.: F.P. 669,872, November 21, 1929.

Table 30. Pumice as a Carrier.

Reaction	Catalyst	Carrier	Observer
Synthesis of $CH_4$ : $CO + 3H_2 \rightarrow CH_4 + H_2O$	Ni + 10% Th.	Pumice.	
Preparation of unsaturated hydrocarbons.	Metallic or oxidic catalysts <i>e.g.</i> , Ni, Co, Cu, or Zn (substituted with an activator such as $CaCO_3$ ).	Pumice.	Dreyfus: F.P. 749,916, August 1, 1933.
Synthesis of $H \cdot CHO$ .	Mixture of oxides.	Pumice or asbestos.	
Preparation of the ethyl ether of acetic acid from acetic acid and alcohol.	$H_3PO_4$ .	Pumice.	Backe, Roberts Co.: Brit. P. 131,088 (1918).
Synthesis of methanol at $500$ to $525^\circ$ .	Sn phosphate or 20 g. $SnCl_4$ + 11.7 g. 90% $H_3PO_4$ .	Large-grained pumice (2 mm.) (20 g.).	Abkin and Medwedew: <i>Zhur. Khim. Prom.</i> , 11, Nr. 1, 30–34 (1934).
Preparation of alcohol from olefins at $125$ – $130^\circ$ under $25$ – $900$ atm. pressure.	Volatile halides $HCl$ , $HI$ , $HBr$ or $CH_3Cl$ , $CCl_4$ , $NH_4Cl$ (–1).	Pumice, silica gel or coke.	E. I. Du Pont de Nemours & Co.: U.S.P. 2,014,740, September 17, 1935.
Decomposition of $C_2H_5OH$ .	Ni.	Pumice.	Walker, Russell and Marschker: <i>J. phys. Chem.</i> , 34, 2554–2566 (1930).



Table 30 (Continued).

Reaction	Catalyst	Carrier	Observer
Decomposition of aliphatic chlorides and bromides, e.g., propyl chloride in the gaseous phase: $C_3H_7Cl + 3O \rightarrow HCl + 3H_2O + 3C$ ; a part of the C is oxidized by $H_2SO_4$ to CO and $CO_2$ .	$H_2SO_4$ , conc.	Pumice.	Senderens and Aboulene: <i>compt. rend.</i> , <b>202</b> , 1548-1550, May 11, 1936.
Oxidation of paraffins in a liquid phase.	$CuSO_4$ .	Pumice.	Schaal: G.P. 32,705 (1884).
Conversion of $CH_4$ to $H \cdot CHO$ .	$Fe_2O_3 + Cr_2O_3$ .	Pumice, asbestos or quartz.	Bakelite Co.: G.P. 411,215.
Oxidation of $CH_3OH$ to $H \cdot CHO$ ; yield, 90%.	Ag.	Pumice.	Gurewitsch and Tschirwinskaja: <i>Zhur. Khim. Prom.</i> , <b>12</b> , Nr. 1, 57-61 (1935).
Oxidation of toluene to benzaldehyde to benzoic acid.	$H_3PO_4$ .	Pumice.	Badische Anilin u. Soda Fabrik: G.P. 408,184 (1920).
Oxidation of benzene to maleic acid at 410 to 450°.	$V_2O_5$ .	Pumice or asbestos.	Salkind and Solotarew: <i>Zhur. Priklad. Khim.</i> , <b>6</b> , 681-684 (1933).
Oxidation of anthracene to anthraquinone.	$H_2VO_4$ .	Pumice.	Badische Anilin u. Soda Fabrik: G.P. 408,184 (1920).
Preparation of hydroaromatic oxides such as methene oxide from chlormenthol and water vapor.	Cu phosphate.	Pumice.	Shering-Kahlbaum (Schoeller, Schwenk, Borgwardt and Kichner): G.P. 574,837, Kl 120, April 20, 1933.
Reduction of CO at ordinary pressure.	Co-Cu-MgO 3 : 1 : 0.45.	Pumice or cane sugar as carrier gives better gas contraction; 60% yield.	Fujimura: <i>J. Soc. Chem. Ind. Japan</i> , <b>34</b> , 227B-229B (1931).
Reduction of aromatic nitro compounds to amines by $H_2$ .	Ni nitrate activated by sulfides or chlorides mixed with metals (Ag, Cu, Fe), or difficultly reducible oxides, e.g., $Al_2O_3$ , MgO, ZnO, $Cr_2O_3$ , silicic acid.	Pumice or kieselguhr.	Furakawa and Kubota: <i>Jap. P.</i> 101,254, July 5, 1933.
Hydrogenation of unsaturated compounds.	Ni-Pd.	Pumice or Al.	Lessing: <i>Austrian P.</i> 82,207, December 27, 1920.
Hydrogenation of fatty oils.	Ni.	Pumice or active charcoal or kieselguhr.	Uno and Saida: <i>J. Soc. Chem. Ind. Japan</i> , <b>30</b> , 107B (1927).
Pressure hydrogenation of fuels at 425° temperature and 200 atm. pressure.	Halide compounds of Mo, U, V, or iodine compounds of Ag, Cu, Ti, Sn, Mn, Ni, and Co or their mixtures.	Pumice, active charcoal, or silicic acid.	I. G. Farbenindustrie A.-G.: F.P. 747,459, June 17, 1933.
Condensation of $C_2H_2$ with primary amines.	$ZnBr_2$ .	Pumice.	G.P. 516,765.
Chlorination of methane with $Cl_2$ or $HCl$ at 450° yield $CH_2Cl$ , 89%, using $CH_4$ ten times in excess.	$CuCl_2 + 1\%$ $CeCl_3$ (4 hrs. treatment with $N_2$ at 150°).	Pumice.	Giordani: <i>Ann. Chim. Applicata</i> , <b>25</b> , 163-173 (1935).
Joint dehydration of $NH_3$ , methyl, ethyl, $n$ -propyl and $n$ -butyl alcohols.	Blue tungsten oxide, alumina, NiO, $CeO$ , $ThO_2$ .	Pumice or silica gel.	Brown and Reid: <i>J. phys. Chem.</i> , <b>28</b> , 1067 (1924).

Table 30 (Continued).

Reaction	Catalyst	Carrier	Observer
Dehydration of butyl alcohol at 350-400°.	90% H <sub>3</sub> PO <sub>4</sub> ; Br added.	Pumice stone.	Komarewsky, Johnstone and Joder: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 2705 (1934). Faworski: (1890).
Catalytic dehydrogenation.	ZnS or CdS.	Pumice.	I. G. Farbenindustrie A.-G.: E.P. 262,120, January 26, 1927.
Dehydrogenation of aromatic hydrocarbons at 500-800°.	Difficultly reducible but fusible metal oxides or cmpds. decomposed into oxides (mixture of potash, ThO <sub>2</sub> and CoO).	Pumice.	I. G. Farbenindustrie A.-G.: Brit. P. 369,613, December 17, 1930.
Dehydrogenation of lower aliphatic alcohols in the gaseous state to ether at 135° and C <sub>2</sub> H <sub>4</sub> ; CH <sub>3</sub> OH to CH <sub>3</sub> OCH <sub>3</sub> at higher temperatures.	Syrupy H <sub>3</sub> PO <sub>4</sub> (dehydrogenates to a high extent); H <sub>2</sub> SO <sub>4</sub> conc.	Pumice.	Senderens: <i>Compt. rend.</i> , <b>192</b> , 1335-1337, June 1, 1931.
Dehydrogenation process.	Conc. solution of mixtures of metallic salts (Cu, Cr, Mg) which are able to split off their volatile acids at higher temperatures without poisoning the catalyst.	Pumice.	Howards and Sons, Ltd. (Blagden and Clark): E.P. 363,776, January 21, 1932.
Preparation of aromatic hydrocarbons unsaturated in the side chain from the corresponding saturated aromatic hydrocarbons under strongly diminished pressure.	Dehydrogenation catalyst mixed with basic Cu, Fe, Ni.	Pumice.	Snida: Austrian P. 132,642, February 25, 1933.

Table 31. Asbestos and Fibrous Material as Carriers.

Reaction	Catalyst	Carrier	Observer
Synthesis of H <sub>2</sub> O.	Pt.	Asbestos.	Emmett and Jones: <i>J. Phys. Chem.</i> , <b>34</b> , 1102-1104 (1930).
Oxidation of NH <sub>3</sub> .	Pt, Os, or Ni.	Fibers.	G.P. 354,212, Kl 12g, June 1, 1922; F.P. 532,343, February 1, 1922.
Oxidation of SO <sub>2</sub> : 2SO <sub>2</sub> + O <sub>2</sub> ⇌ 2SO <sub>3</sub>	Pt.	Asbestos.	Petrie: Brit. P. 590 (1852). Winkler: G.P. 4,566 (1898).
Oxidation of SO <sub>2</sub> : 2SO <sub>2</sub> + 1/2O <sub>2</sub> + H <sub>2</sub> O → H <sub>2</sub> SO <sub>4</sub>	Pt (vapors condensed in a vacuum); the same activity as ordinary Pt on asbestos.	Asbestos.	Dankow, Joffe, Kotschetkow and Perewesentzew: <i>Khim. Zhur. S.S.S.R.</i> , <b>4</b> , 334-342 (1933).
Oxidation of SO <sub>2</sub> .	Pt or metals of the Pt group (activator, iron sulfate).	Asbestos.	E. I. Du Pont de Nemours & Co. (J. H. Perry): U.S.P. 1,914,458, June 20, 1933.
Conversion of CH <sub>4</sub> to H · CHO.	Fe <sub>2</sub> O <sub>3</sub> + Cr <sub>2</sub> O <sub>3</sub> .	Asbestos, pumice or quartz.	Bakelite Co.: G.P. 411,215.
Synthesis of: HCOOH + NH <sub>3</sub> → HCOONH <sub>4</sub> .	Pt (110°).	Asbestos.	Dubose: <i>Rev. des Produits Chim.</i> , <b>27</b> , 433-434 (1924).
Thermal decomposition of cellulose under hydrogenation conditions.	Fe vanadate, Ni oxalate.	Fibers.	Bowen, Shotwell and Nash: <i>J. Soc. Chem. Ind.</i> , <b>44</b> , 507-511 (1925).
Oxidation of: CH <sub>3</sub> OH + 1/2 O <sub>2</sub> → HCHO + H <sub>2</sub> O	Pt.	Asbestos.	M.L.B. (Trillat): G.P. 55,176 (1889).

Table 31 (Continued).

Reaction	Catalyst	Carrier	Observer
Oxidation of: $C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O$	Light metals or Cu.	Asbestos or pumice.	Bayer Co.: G.P. 346,520 (1917).
Oxidation of $CH_3OH$ .	Ag.	Asbestos.	Blank: G.P. 228,697 (1908).
Oxidation of $CH_3OH$ : $CH_3OH + \frac{1}{2}O_2 \rightarrow HCHO + H_2O$	$AgNO_3$ (impregnated, dried, treated with dilute formic acid).	Porous, inert material such as asbestos.	Soc. Ann. Ch. Mildé Pils and Cie: Swiss. P. 169,857, September 17, 1934.
Oxidation of acetaldehyde of acetic acid.	Pt.	Asbestos.	Dreyfus: F.P. 487,412 (1918).
Oxidation of benzene to maleic acid at 410–450°.	$V_2O_5$ .	Asbestos or pumice.	Salkind and Solotarew: <i>Zhur. Priklad. Khim.</i> , 6, 681–684 (1933).
Oxidation of toluene.	Iron vanadate and iron oxide.	Asbestos.	Adam, Sherman and Cuckney (The Peoples Gas, Light and Coke Co.): E.P. 331,535, July 31, 1930.
Reduction of nitrobenzene at 260°.	Tl oxide.	Asbestos.	Brown, Chester Bros. and Etzel: <i>J. Phys. Chem.</i> , 32, 456–458 (1928).
Reduction of CO.	Ni.	Asbestos.	Pieters: <i>Chem. Weekblad</i> , 28, 209–210 (March 28, 1931).
Continuous hydrogenation of unsaturated oils and fats.	Ni.	Wool.	Belton: E.P. 162,370, May 23, 1921.
Hydrogenation processes.	$CCl_4$ , $CHCl_3$ , or a reducing substance.	Asbestos or kieselguhr.	Schicht: Austrian P. 93,481, July 10, 1923.
Hydrogenation of pyridine.	10% Pd.	Asbestos.	Zelinsky and Borissoff: <i>Ber.</i> , 57, 150–153 (1924).
Hydrogenation.	Ni, Cu, Co and Fe nitrates.	Asbestos.	Victoria: <i>Anales asoc. quim. argentina</i> , 12, 405–420 (1925).
Hydrogenation of olefins at 150–250°.	$ThO_2$ or Pt, Au, Cu, W or their compounds.	Basic substances; asbestos, pumice, charcoal or active silica.	Dreyfus: E.P. 389,136, April 6, 1933.
Hydrogenation of the furan nucleus; almost quantitative yield of pure tetrahydrosilven.	Os.	Asbestos.	Zelinsky and Schuikin: <i>Doklady. Akad. Nauk. S.S.S.R.</i> , 60, 65 (1933).
Determination of gaseous olefins or hydrogen through catalytic hydrogenation.	Melted metallic nickel prepared from Ni nitrate.	Asbestos (purified by $HNO_3$ ).	McMillan, Cole and Ritchie: <i>Ind. Eng. Chem.</i> , (Anal. Ed.), 8, 105–107 (1936).
Dehydrogenation of cyclohexane.	Pd.	Asbestos.	Balandin: <i>Z. physik. Chem.</i> (B), 19, 451–461 (1932).
Dehydrogenation of pyrrole to a mixture of pyrrol and pyrrolidine.	Pt (8 cm. layer).	Asbestos.	Wibaut and Proost: <i>Rcc. trav. Chim. Pays-Bas</i> , 52, 333–336 (1933).
Condensation with dehydration; preparation of diethyl aniline from aniline and alcohol at 370–375°.	$ThO_2$ .	Asbestos.	Chandra: <i>J. Ind. Chem. Soc.</i> , 5, 383 (1928).
Dehydration of hydrocarbons.	Pt.	Asbestos.	I. G. Farbenindustrie A.-G.: E.P. 357,749, October 22, 1931.
Preparation of ketenes at 700°.	Cr, Mn, Al, Ca, Ba, Sr, Mg and Ag sulfates; $Al_2(SO_4)_3$ , the most active.	Asbestos or portland cement diluted with $H_2SO_4$ .	Ketoid Co.: E.P. 237,573, September 16, 1925.
Catalytic influence in self-ignition processes for benzene without contact at 690°; the ignition point was reduced by the contact to 160°.	50% Pd.	Asbestos.	Eckert and Jentzsch: <i>Ang. Chem.</i> , 46, 659–662, October 21, 1933.

Table 32. Earths as Carriers.

Reaction	Catalyst	Carrier	Observer
Oxidation of $\text{NH}_3$ .	Pt or Cr; Fe < Sr < U < Mn < Ce < Mo < W < Cr.	Puzzolana earth.	G.P. 545,427, Kl 12i, February 29, 1932. Marmier: <i>Compt. rend.</i> , 199, 868-869 (1934).
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ .	$\text{Ti}_2\text{O}_3$ ; $\text{Ag}_2\text{O}$ ; $\text{V}_2\text{O}_5$ 1/4 : 1 : 1	Diatomaceous earth, kieselguhr, or celite pieces.	Selden Co. (Piedler and Jaeger): U.S.P. 1,945,267, January 30, 1934.
Preparation of butene from butanols.	Activated alumina 30% $\text{H}_3\text{PO}_4$ (89%) 80% $\text{H}_3\text{PO}_4$ (89%) 50% $\text{H}_3\text{PO}_4$	Diatomaceous earth.	Ipatieff and Schaad: U.O.P. (1933-1934).
Isomerization of butenes.	Solid $\text{H}_3\text{PO}_4$ 30% $\text{H}_3\text{PO}_4$ (89%)	Diatomaceous earth.	Ipatieff and Schaad: U.O.P. (1933-1934).
Preparation of <i>p</i> -cymol from tertiary alcohols at 160-220°.	Dehydrating catalyst.	Fuller's earth, kieselguhr or active charcoal or $\text{Al}_2\text{O}_3$ .	Bennett and Frazer: U.S.P. 1,893,879, January 10, 1933.
Preparation of camphor oils (cineol).		Japanese acid earth.	Bashish Ono and Shuei Miyazaki: <i>Bull. Chem. Soc. Japan</i> , 2, 207-209.
Cracking of petroleum oil.	$\text{Fe}_2\text{O}_3$ , Ni, NiO.	Infusorial earth or pumice.	Osterstrom and Wagner: F.P. 654,782, April 10, 1929; Austrian P. 13,623, January 22, 1929.
Preparation of light hydrocarbons from petroleum oils at 200° by hydrogenation.	Ni.	Fuller's earth.	Gray Processes Corp. (Gray): U.S.P. 1,878,580, September 20, 1932.
Catalytic reaction.	Vanadium oxide (melted).	Infusorial earth.	E. I. Du Pont de Nemours & Co. (Gibbs): U.S.P. 1,463,206, July 31, 1923.
Catalytic reaction.	$\text{Al}_2\text{O}_3$ ( $\text{NH}_3$ salt added to the mixture to loosen it).	Infusorial earth with 10-15% of $\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ .	Verein f. Chemische u. Metallurgisch Produktion: F.P. 688,561, August 26, 1930.
Hydrogenation of fuels at intermittent pressure.	Active Fe ppt.	Infusorial earth.	I. G. Farbenindustrie A.-G.: E.P. 381,367, October 27, 1932.
Pressure hydrogenation of fuels: coal, pitch.	$\text{MgCl}_2$ , carnallite, $\text{NaHSO}_4$ , or $\text{NaOH}$ together with Zn or Al dust (substances develop $\text{H}_2$ on heating).	Infusorial earth, bauxite or aluminum hydrosilicate.	Kern: U.S.P. 1,852,709, April 5, 1932.
Polymerization of gaseous hydrocarbons ( $\text{C}_2\text{H}_4$ , $\text{C}_3\text{H}_4$ ) into liquid hydrocarbons at 260-540° and 40-120 atm. pressure.	$\text{AlCl}_3$ , $\text{AlBr}_3$ , metal halides, Pd-Pt sponge, finely dispersed alloys, metals of the 8th group.	Fuller's earth or silica gel or active coal.	Pure Oil Co.: F.P. 680,038, April 24, 1930.
Polymerization of butylenes.	30% solid $\text{H}_3\text{PO}_4$ .	Diatomaceous earth.	Ipatieff and Schaad.
Polymerization of propylene under 10 kg. per sq. cm.	$\text{H}_3\text{PO}_4$ and $\text{P}_2\text{O}_5$ (1 : 1)	Diatomaceous earth or silica gel or activated charcoal or petroleum coke.	Ipatieff and Schaad: (1933).
Chlorination of propylene.	$\text{Fe}_2\text{O}_3$ .	Florida earth or porous and adsorbing $\text{Al}_2\text{O}_3$ or $\text{SiO}_2$ .	Gayer: <i>Ind. Eng. Chem.</i> , 25, 1122-1127 (1933).
Chlorination of amylene and ethylene.	80% $\text{H}_3\text{PO}_4$ .	Diatomaceous earth.	Ipatieff and Schaad: (1933).
Dehydration of isobutylcarbinol.	(The carrier acts as a catalyst).	40% infusorial earth + 30% ton earth and 30% corn flour.	Yose Puyal: <i>Anales Soc. Espanola Fis. Quim.</i> , 20, 81-83 (1922).
Desulfurization of hydrocarbon oils.	$\text{CuO}$ , $\text{CuCl}_2$ , $\text{HgCl}_2$ , $\text{FeCl}_3$ .	Fuller's earth.	Bennett-Clark Co. (Hoover): U.S.P. 2,042,050, August 10, 1935; U.S.P. 2,042,051 to 2,042,054, May 26, 1936.

Table 33. Kieselguhr as a Carrier.

Reaction	Catalyst	Carrier	Observer
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	V or Pt cmpds.	Kieselguhr plus an alkali silicate solution e.g., $\text{SiO}_2 + (\text{NH}_4)_2\text{CO}_3$ ppt.; a gelatinous mixture formed and dried to obtain highly porous product.	Alexander, Crawford and Challenor (Imperial Chemical Industries, Ltd., London); E.P. 337,761, December 4, 1930.
Manufacture of $\text{H}_2\text{SO}_4$ .	Pt.	Kieselguhr (strongly acid silicates, high in content of silicic acid; when heated with metal oxides or salts readily form silicates; basic ingredients removed from reaction mixture by treatment with mineral acid).	Verein f. Chemische u. Metallurgisch Produktion: Austrian P. 123,811, July 25, 1931.
Catalytic reaction.	Freshly ppt. $\text{Al}_2\text{O}_3$ and iron oxide.	Kieselguhr; after molding and drying the catalyst-carrier is treated with $\text{H}_2\text{SO}_4$ or $\text{HCl}$ .	Verein f. Chemische u. Metallurgisch Produktion: Swiss P. 148,474, October 1, 1931.
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ .	$\text{Ti}_2\text{O}_3 : \text{Ag}_2\text{O} : \text{V}_2\text{O}_5$ (1/4 : 1 : 1).	Kieselguhr, diatomaceous earth or pieces of celite (250 vol. by part silocel C22).	Selden Co. (Fiedler and Jaeger); U.S.P. 1,945,267, January 30, 1934.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	316 parts kieselguhr heated to red heat, mixed with 21 parts tragacanth to which is added 50 p. $\text{NH}_4\text{VO}_3$ and 56 p. $\text{KOH}$ (so much water is present that the mass may be remolded).	Kieselguhr.	General Chemical Co. (H. Joseph); U.S.P. 2,029,376, February 4, 1936.
Preparation of oxy-alkyl amines.	Ni.	Kieselguhr.	I. G. Farbenindustrie A.-G. (Schlichting); G.P. 573,983, Kl 12g. April 8, 1933.
Benzene synthesis: $\text{CO} : \text{H}_2$ .	Co-Th.	Kieselguhr.	Fischer and Koch: <i>Brennstoff-Chemie</i> , 13, 61-68, February 15, 1932.
Thermal decomposition of methane, using electric discharge at $1050^\circ$ ; 3.5% yield $\text{C}_2\text{H}_2$ .	V (Mo, Ni): coarse catalysts: Zr ore, coke, active coal, kaolin.	Kieselguhr.	Kljukwin and Kljukwina: <i>Russ. Khim. Tverdogo Topliva</i> , 6, 130-146 (1935).
Reduction of aromatic nitro-compounds to amines by $\text{H}_2$ .	Ni nitrate activated by sulfides or chlorides mixed with metals (Ag, Cu, Fe), or difficultly reducible oxides ( $\text{Al}_2\text{O}_3$ , $\text{MgO}$ , $\text{Cr}_2\text{O}_3$ , $\text{ZnO}$ ) with silicic acid.	Kieselguhr or pumice.	Furakawa and Kubota: Japan P. 101,254, July 5, 1933.
Reduction of higher alcohols (primary and secondary alcohols obtained at high pressures hydrogenated to alcohols free from aldehydes and ketones).	Ni.	Kieselguhr (Cu chromite, Cu-Ba chromite).	Morgan, Douglas and Hardy: <i>J. Soc. Chem. Ind.</i> , 52, 518-519 (1933).
Hydrogenation of unsaturated organic cmpds.	Boric acid compounds of Ni.	Kieselguhr.	Müller Speisefettfabrik: G.P. 352,431, Kl 12o, April 27, 1922.
Hydrogenation processes.	Metallic salts of volatile organic acids ppt.	Kieselguhr.	Schicht: Austrian P. 93,481, July 10, 1923.

Table 33 (Continued).

Reaction	Catalyst	Carrier	Observer
Hydrogenation of fatty acids at 180°.	Zn, Pb, Ag, Sb.	Kieselguhr.	
Hydrogenation of fatty acids.	20% Ni.	Kieselguhr.	Kailan and Stüber: <i>Monatsh.</i> , <b>62</b> , 90-100 (1932).
Hydrogenation of CO under atmospheric pressure.	Fe-Cu ppt. from Fe and Cu nitrate solution.	Kieselguhr acts unfavorably.	Antheaume: <i>Ann. combustibles liquides</i> , <b>10</b> , 473-507, May-June, 1935.
Hydrogenation of maleic and fumaric acids and sodium cinnamate.	Pd.	Kieselguhr, sugar charcoal or BaSO <sub>4</sub> , bone charcoal, etc.	Sabalitschka and Moses: <i>Ber.</i> , <b>60B</b> , 786 (1927).
Hydrogenation of cinnamic acid and its methyl, ethyl, propyl, and n-butyl, benzyl and phenyl ester.	Ni (pure Ni and Ni on silicic acid gel decrease greatly the hydrogenation velocity).	Kieselguhr.	Kailan and Hardt: <i>Monatsh.</i> , <b>58</b> , 307-368 (1931).
Hydrogenation of aromatic hydrocarbons under high pressure.	Ni.	Kieselguhr.	Shoorel, Tulleeurs and Waterman: <i>J. Inst. Pel. Tech.</i> , <b>18</b> , 179-182 (1932).
Hydrogenation of primary aromatic amines at 175-250° under high pressure; hydrogenation of aniline at 175° for 5 to 8 hrs. under 150-240 atm. pressure.	Ni solution impregnated, then treated with basic carbonate; NiCO <sub>3</sub> obtained is reduced.	Kieselguhr.	Goodyear Tire & Rubber Co.: F.P. 750,903, August 22, 1933.
Hydrogenation of naphthalene to tetrahydronaphthalene.	NaK or NaK <sub>2</sub> .	Kieselguhr.	Co. de Produits Chim. et Electr. Froges et Camargue: F.P. 609,786, August 24, 1926.
Oil hardening.	Pd.	Kieselguhr.	Verein Chem. Werke A.-G. (Paal): G.P. 236,488, July 7, 1911.
Hydrogenation of oil at 180°.	Ni.	Kieselguhr.	Armstrong and Hilditch: <i>Proc. Roy. Soc. London (A)</i> , <b>99</b> , 490-495 (1920).
Hydrogenation of fatty oils.	Ni.	Kieselguhr, or activated charcoal or pumice.	Uno and Saida: <i>J. Soc. Chem. Ind. Japan</i> , <b>30</b> , 107B (1927).
Conjugated hydrogenation of soybean oil with C <sub>2</sub> H <sub>5</sub> OH at 250°.	Ni.	Kieselguhr.	Pastuscheni: <i>Masloboino Zhivoc Delo</i> , <b>9</b> , No. 1, 21-22 (1933).
Hydrogenation of fats.	Ni.	Kieselguhr.	Kaiser: U.S.P. 1,004,035 (1911); U.S.P. 1,008,474 (1911).
Dehydrogenation of isoborneol (preparation of camphor).	Zn, Cu, Ag, or Cd (their hydroxides soluble in excess of NH <sub>3</sub> ), e.g., Cu(NO <sub>3</sub> ) <sub>2</sub> , Zn(NO <sub>3</sub> ) <sub>2</sub> , Cd(NO <sub>3</sub> ) <sub>2</sub> , AgNO <sub>3</sub> alone or in a mixture.	Kieselguhr.	E. I. Du Pont de Nemours & Co.: E.P. 392,134, June 1, 1933.

Table 34. Chamotte as a Carrier.

Reaction	Catalyst	Carrier	Observer
Oxidation of SO <sub>2</sub> to SO <sub>3</sub> .	Ag vanadate.	Chamotte.	Adadurow and Borskow: <i>Zhur. Khim. Prom.</i> , <b>6</b> , 805-807 (1928).
Catalytic reactions.	Acidified vanadium salt solution replaced by iron oxide and boiled with the carrier or V <sub>2</sub> O <sub>5</sub> is ppt. with AgNO <sub>3</sub> solution and the carrier boiled in the acidified vanadium salt solution.	Chamotte.	Adadurow and Borskow: <i>Russ. P.</i> 16,656, September 30, 1930.

Table 34 (Continued).

Reaction	Catalyst	Carrier	Observer
Oxidation of butyl aldehyde to butyric acid.	Mn butyrate.	Chamotte.	Legg and Adam: Brit. P. 173,004 (1920); U.S.P. 1,418,448 (1921).
Solidification of fats.	Cu, Ni, Fe, Co, Pt melted together.	Chamotte.	Harter and Meyer: G.P. 401,010, Kl. 23d, August 25, 1924.
Hydrogenation of commercial phenols in the vapor phase.	Ni formate; 10-15% Ni nitrate (impregnated).	Chamotte.	Snelling: U.S.P. 122,811.

Table 35. Cements as Carriers.

Reaction	Catalyst	Carrier	Observer
Oxidation of CO: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	Fe(OH) <sub>3</sub> mixed with Na <sub>2</sub> CO <sub>3</sub> .	Dehydrated binding agent, e.g., cement (serves to solidify the catalyst) (rotating drum used).	Non-Poisonous Gas Holding Co., Ltd.: F.P. 777,546, February 22, 1935.
Hydrogenation and cracking of oils.	Fe oxide.	Cement with catalyst shaped into sticks with a wooden stick or sawdust in the middle.	Gyro Process Corporation (Harnsberger and Smith): U.S.P. 1,873,707 (1932) and U.S.P. 1,874,743 (1932).
Catalytic treatment of gases.	Catalyst.	Hydraulic binding material stabilized by heating before use; molded without pressure.	Nitrogen Ges. (Berlin): G.P. 312,726, Kl. 12g. Group 2 (1919).
Preparation of H <sub>2</sub> from hydrocarbons, saturated or unsaturated and higher than CH <sub>4</sub> , below 1000° by action of water vapor or CO <sub>2</sub> .	Fe, Co, Ni.	Hydraulic binding materials.	I. G. Farbenindustrie A.-G.: F.P. 729,119, July 19, 1932.

Table 36. Clay as a Carrier.

Reaction	Catalyst	Carrier	Observer
Dehydration of alcohols.	Ni, Cu or Ag; CuO, CuO+Ag <sub>2</sub> O, Cr <sub>2</sub> O <sub>3</sub> , MnO, ZnS also selenides and phosphides.	Glassy clay.	I. G. Farbenindustrie A.-G.: E.P. 313,426, July 11, 1929.
Hydrogenation of oils.	Ammonium nickel oxide or hydroxide (impregnated).	Acid white clay.	Tonaka, Miroshita, Maeda and Heno: Jap. P. 100,179, March 20, 1933.
Condensation of C <sub>2</sub> H <sub>2</sub> with CH <sub>3</sub> COOH; not only is the reaction accelerated, but the yield is tripled.	Mercury sulfate (prepared from HgO in CH <sub>3</sub> COOH by means of H <sub>2</sub> SO <sub>4</sub> with 50% SO <sub>3</sub> ).	Japanese acid clay.	Tsutomu Kuwata and Osmu Kato: J. Soc. Chem. Ind. Japan, Suppl., 39, 127B-128B (1936).
Desulfurization of hydrocarbon oils.	5% CuCl <sub>2</sub> and 5% KMnO <sub>4</sub> 5% CuCl <sub>2</sub> 1-8% HgCl (CoCl <sub>2</sub> , CdCl <sub>2</sub> ) + 1-30% CuCl <sub>2</sub>	90% dry ton. 95% dry ton, the remainder, dry ton.	Bennett-Clark Co. (Hoover): U.S.P. 2,042,050, August 10, 1935; U.S.P. 2,042,051-2042,054, May 26, 1936.

Table 37. Kaolin as a Carrier.

Reaction	Catalyst	Carrier	Observer
Decomposition of CH <sub>4</sub> : $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$	Fe, Co, Ni.	Kaolin.	Nauss: G.P. 226,609 (1909).
Decomposition of hydrocarbons with water vapor, CO <sub>2</sub> , O <sub>2</sub> or air in H <sub>2</sub> -CO or H <sub>2</sub> -CO-N <sub>2</sub> mixtures.	Metals of the Fe group.	Kaolin: unburned natural Al or artificial Al silicate.	I. G. Farbenindustrie A.-G. (Wietzel and Hennicke): G.P. 554,551, Kl. 12i, July 11, 1932.

Table 37 (Continued).

Reaction	Catalyst	Carrier	Observer
Splitting of aliphatic mono-brom derivatives: $C_nH_{2n+1}Br \rightarrow HBr + C_nH_{2n}$	$ThO_2, Al_2O_3$	Kaolin.	Senderens: <i>Compt. rend.</i> , 200, 2137-2139 (1935).
Thermal decomposition of $Na_2SO_4$ : (1) 54-77% yield. (2) 8-13% yield.	$SiO_2$	Kaolin. (1) $Na_2SO_4$ : kaolin 1:3 (2) $Na_2SO_4$ : kaolin 4:1	Fialkow and Schargorodsky: <i>Ukrain. Akad. Nauk., Zapiski Inst. Khim.</i> , 2, 269-283 (1935).
Dehydration of ethyl alcohol.	$H_2SO_4$	Glowed kaolin.	Deymann: (1795); refer to <i>Bull. Soc. Chim.</i> , 2, 1000 (1935).
Dehydration of $NH_3$ and $C_2H_5OH$ .	Blue tungsten oxide ( $WO_3$ ).	Kaolin.	Briner and Gemdillon: <i>Helv. Chim. Acta</i> , 14, 1283 (1931).
Dehydration of alcohol.		Glowed (at 750-800°) kaolin (water content, 1%); activated by $HNO_3$ (33%) in amount of 62.5% at 60-80°; replaced by 12-25% $NH_4OH$ (ppt. dried at 100-120°).	Larin and Tscherepnjew: <i>Russ. P.</i> 41,504, February 28, 1935.
Hydrogen prepared from hydrocarbons passed with water vapor, $O_2$ or $CO_2$ .	Mixture Fe, Ni, or Co.	Kaolin or bauxite.	I. G. Farbenindustrie A.-G.: F.P. 677,826; E.P. 323,855, February 6, 1930.
Preparation of hydrogen by the decomposition of hydrocarbons in the presence of water vapor, $CO_2$ or $O_2$ .	Fe, Ni, Co in a mixture with Al compds. containing $O_2$ and one or more elements, such as Si, H <sub>2</sub> , C, B, P.	Kaolin or Al silicate or bauxite.	I. G. Farbenindustrie A.-G.: E.P. 323,855, February 6, 1930.
Catalytic reactions.	A solution of Pd compound; after impregnating the carrier, it is heated in a $H_2$ stream saturated with formaldehyde vapors.	Mixture of kaolin and charcoal (rings).	Alexejewski: <i>Russ. P.</i> 24,389, December 31, 1931.
Catalytic reactions.	Catalyst.	Kaolin or white clay (free of $SiO_2$ ) + organic cement such as mazut or tar or distillation residue of any kind; mass treated with a reducing and oxidizing flame.	Comp. Intern. pour la Fabrication des Essences de Petroles: Austrian P. 123,377, June 25, 1931.

Table 38. Porous Ceramic Materials as Carriers.

Reaction	Catalyst	Carrier	Observer
Oxidation of $SO_2$ : $2SO_2 + O_2 \rightarrow 2SO_3$ .	Pt.	Contact.	G.P. 440,338, Kl. 12i, December 2, 1927.
Oxidation of $SO_2$ : $2SO_2 + O_2 \rightarrow 2SO_3$ .	Pt solution.	Porous ceramics or $MgSO_4$ .	Artner: E.P. 265,938, April 6, 1927.
Synthesis of $NH_3$ : $N_2 + 3H_2 \rightarrow 2NH_3$ .	Alkali Fe cyanide.	Porous carrier.	Clancy: U.S.P. 1,363,393, December 28, 1930.
Oxidation of CO: (1) $CO + H_2O \rightarrow CO_2 + H_2$ . (2) $2CO + O_2 \rightarrow 2CO_2$ .	Fe-containing substances,	Carrier.	Fourneau and Ribas: <i>Bull. Soc. Chim.</i> , 4 (39), 1587-1589 (1926).
Oxidation of $CH_3OH$ : $CH_3OH + 1/2O_2 \rightarrow HCHO + H_2O$ .	$AgNO_3$ (impregnated) (dried and treated with dilute formic acid).	Porcelain (porous, inert material such as asbestos).	Soc. Ann. Ch. Mildé Pils. et Cie: Swiss. P. 169,857, September 17, 1934.



Table 38 (Continued).

Reaction	Catalyst	Carrier	Observer
Oxidation of toluene in a vapor phase.	Higher oxides of Mo or V in an acid solution with Fe chromium and difficultly reducible oxides.	Carrier.	Bogdanow: Russ. P. 38,633, September 30, 1934.
Dehydration of phenols at 350-525°.	Th (heated electrically in the tube).	Glazed porcelain tube.	Briner and Bron: <i>Helv. Chim. Acta</i> , <b>15</b> , 1234-1241 (1932).
Preparation of acetone from acetic acid.	V, 2A-steel.	Ceramic mass.	Deutsche Gold u. Silber Scheideanstalt (Roessler, Walter and Schultz): G.P. 581,047, Kl 120, July 20, 1933.
Hydrogenation of oils.	Pd.	Inert carriers.	Vereinigte Chemische Werke A.-G.: G.P. 236,488, August 6, 1910; Brit. P. 18,642 (1911).
Hydrogenation of fats.	Pd.	Carriers.	Vereinigte Chemische Werke A.-G. (Paal): G.P. 236,488 (1910). Schlink and Co. A.-G. (Paal): G.P. 252,320 (1911); Brit. P. 5,188 (1911).
Hydrogenation of maleic acid in an aqueous solution; hydrogenation of cyclohexane in an alcoholic solution at 15-20 atm. pressure.	Metallic Rh.	Ceramic material (active for the dehydrogenation of alcohol; in itself, a weak catalyst).	Platonow, Anissimow and Krascheninnikow: <i>Ber.</i> , <b>68</b> , 761-765, May 8, 1935.
Conversion of hydrocarbons and water vapor in the preparation of H <sub>2</sub> .	Alloys with 20% Ni and 24% Cr.	Inert carriers.	Tröger: <i>Petroleum</i> , <b>28</b> (34), 9-1, August 24, 1932.
Preparation of alkyl chlorides at 220°.	Less than 50% H <sub>3</sub> PO <sub>4</sub> .	Carrier.	Walker Gesellschaft f. Elektr. Industrie G.m.b.H. (Ernst): G.P. 583,497, Kl 120, September 4, 1933; add to G.P. 541,566.

Table 39. Alumina as a Carrier.

Reaction	Catalyst	Carrier	Observer
Preparation of acetone from acetic acid.	Oxides or hydroxides.	Melted Al, Ca or Ba.	Stockholm Superfosfat Fabriks Aktiefolag: E.P. 171,391, December 31, 1921.
Dehydration of <i>o</i> -hexahydro cresol.	CuO.	Alumina.	Ipateiff and Rutala: <i>J. Russ. Phys.-chem. Soc.</i> , <b>44</b> , 1692 (1912).
Dehydration of NH <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> OH.	Th.	Alumina or silica gel.	Briner and Gemdillon: <i>Helv. Chim. Acta</i> , <b>14</b> , 1283 (1931).
Dehydration of alcohols.	CuSO <sub>4</sub> impregnated.	Al <sub>2</sub> O <sub>3</sub> .	I. G. Farbenindustrie A.-G.: F.P. 679,998.
Dehydration of butyl alcohol at 250°.	90% H <sub>3</sub> PO <sub>4</sub> with Br added.	Al <sub>2</sub> O <sub>3</sub> .	Komarewsky, Johnstone and Joder: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 2905 (1934).
Hydrogenation of unsaturated compounds.	Ni-Pd.	Al or pumice.	Lessing: Austrian P. 82207, December 27, 1920.

Table 39 (Continued).

Reaction	Catalyst	Carrier	Observer
Preparation of higher ketones from aliphatic alcohols (acetone) at 150–400°.	15% Cu formate + 1.8% MoO <sub>3</sub> .	Active alumina (treated with a mixture of air and water vapor at 450°).	Deutsche Gold u. Silber Scheideanstalt (Roessler): F.P. 741,385, February 10, 1933.
Dehydrogenation process.	CuSO <sub>4</sub> , MnO, or CoO.	Glazed alumina.	I. G. Farbenindustrie A.-G.: F.P. 679,998, April 23, 1930.
Dehydrogenation of cyclohexane.	Ni.	Al <sub>2</sub> O <sub>3</sub> .	Balandin: <i>Z. phys. Chem.</i> B, 19, 451–461 (1932).
Dehydrogenation of 43% crude oil with a high percentage of aromatic hydrocarbons at 160°.	Ni.	Al <sub>2</sub> O <sub>3</sub> .	Zelinsky and Schuikin: <i>Zhur. Obshchei Khim.</i> , 4 (66) 901–905 (1934).
Dehydrogenation of a fraction of Surachan benzene (Baku) rich in hydroaromatics.	Ni.	Al <sub>2</sub> O <sub>3</sub> .	Zelinsky and Schuikin: <i>Izvest. Akad. Nauk. S.S.S.R.</i> , 7, 229–237 (1935).

Table 40. Bauxite as Carrier.

Reaction	Catalyst	Carrier	Observer
$C_2H_2 + NH_3 \rightarrow CH_3CN + H_2$ .	ThO <sub>2</sub> , ZrO <sub>2</sub> .	Bauxite, permutite or mud ore.	Rhenania Verein Chem. Fabrik: G.P. 367,538 (1918). I. G. Farbenindustrie A.-G.: G.P. 477,049 (1927).
Preparation of H <sub>2</sub> from hydrocarbons.	Mixture Fe, Ni, or Co.	Bauxite or kaolin.	I. G. Farbenindustrie A.-G.: Brit. P. 323,855, F.P. 677,826.
Preparation of H <sub>2</sub> by decomposition of hydrocarbons in the presence of water vapor, CO <sub>2</sub> , or O <sub>2</sub> .	Fe, Ni, Co in a mixture with Al cmpds. containing O <sub>2</sub> and one or more elements such as Si, H <sub>2</sub> , C, B, P.	Bauxite, kaolin, or Al silicate.	I. G. Farbenindustrie A.-G.: E.P. 323,855, February 6, 1930.
Dehydration of isoamyl alcohol.	NaPO <sub>3</sub> .	Bauxite.	I. G. Farbenindustrie A.-G.: E.P. 367,892, March 24, 1932.
Preparation of acetic anhydride from acetic acid.	Fe and other metals assisting in the removal of side reactions.	Bauxite and pumice boiled with 5% tartaric acid and extracted with acetic acid.	British Celanese, Ltd. (Bader): E.P. 366,973, March 10, 1932.
Pressure hydrogenation of fuels such as coal, pitch.	MgCl <sub>2</sub> , carnallite, NaHSO <sub>4</sub> or NaOH, together with Zn or Al dust.	Bauxite or infusorial earth; Al hydrosilicates.	Kern: U.S.P. 1,852,709, April 5, 1932.
Cracking method by filtering through contact at 150–300°.	AlCl <sub>3</sub> (ZnCl <sub>2</sub> , MgCl <sub>2</sub> , CuO).	Bauxite (activated by grinding with water and heating to a red glow).	Catalysts, Ltd. (Gifford): E.P. 945,727 and E.P. 445,757, May 14, 1936; F.P. 797,947, May 6, 1936.

Table 41. Salts as Carriers.

Reaction	Catalyst	Carrier	Observer
Oxidation of SO <sub>2</sub> to SO <sub>3</sub> .	Pt solution (impregnated).	MgSO <sub>4</sub> · 7H <sub>2</sub> O, or porous ceramic materials.	Artner: E.P. 265,938, April 6, 1927.
Oxidation of SO <sub>2</sub> .	Pt (0.3%); 1% Fe sulfate; small amounts of a salt of alkaline earth metals, or Fe, Th, Ta or Ce may serve as activators.	MgSO <sub>4</sub> (98.7%).	E. I. Du Pont de Nemours & Co.: U.S.P. 1,914,835, June 20, 1933.

Table 41 (Continued).

Reaction	Catalyst	Carrier	Observer
Manufacture of $\text{H}_2\text{SO}_4$ from 2% $\text{SO}_2$ activated at $350^\circ$ .	Pt (plating with Pt occurs with 0.1% $\text{Pt}(\text{NH}_4)_2\text{Cl}_2$ solution).	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (grained mass 2.5–3.5 mm.).	Mototaro Matski and Ken-ichi Oda: <i>J. Soc. Chem., Ind. Japan</i> ; <b>38</b> , 148B–51B (1935).
Manufacture of $\text{H}_2\text{SO}_4$ .	Pt.	75% $\text{MgSO}_4$ , 10–15% $\text{Al}_2(\text{SO}_4)_3$ and 10–15% $\text{Fe}_2(\text{SO}_4)_3$ .	Grasselli Chemical Co. (Perry and Ridler): U.S.P. 2,031,987, February 25, 1936.
Oxidation of methane: $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	$\text{Ni}(\text{NiO})$ .	$\text{MgO}$ .	Badische Anilin u. Soda Fabrik: G.P. 296,866 (1912).
Oxidation of methane: (1) $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ (2) $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$ (3) $2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 2\text{H}_2$	$\text{Ni}(\text{NiO})$ $\text{Ni} + \text{Al}_2\text{O}_3$ .	$\text{MgO}$ .	Badische Anilin u. Soda Fabrik: G.P. 306,301 (1914).
Oxidation of CO.	$\text{FeCO}_3 + 0.7\% \text{ K}_2\text{Cr}_2\text{O}_7$ (highly active at $500^\circ$ ; does not decompose as readily as pure siderite; Co alone very active, but not very stable).	$\text{MgO}$ (increases stability).	Iwanowsky, Braude and Panina: <i>Zhur. Khim. Prom.</i> , <b>2</b> , 37–44 (1934).
Decomposition of $\text{CH}_4$ .	Fe, Co, Ni, or Cu.	$\text{MgO}$ or $\text{Al}_2\text{O}_3$ .	Badische Anilin u. Soda Fabrik: Russ. P. 24,386 (1911).
Solidification of fats.	Pd.	$\text{MgO}$ .	Paal and Karl: <i>Ber.</i> , <b>30</b> , 69 (1913).
Hydrogenation of coal in the preparation of hydrocarbons at 50 atmospheres pressure.	Ag, Au, Rh, Os, Pd, Ir, or Pt or their cmpds.	Magnesia or magnesite.	I. G. Farbenindustrie A.-G.: E.P. 275,670, October 5, 1927; E.P. 295,587, October 10, 1928.
Hydrogenation and dehydrogenation processes.	$\text{Ni}(\text{NO})_2$ or solutions; Cu formate solution; A mixture of $\text{Cu}(\text{NO}_3)_2 + \text{Mn}(\text{NO}_3)_2$ .	$\text{MgO}$ . Granulated Mg. Granulated CaO (the carrier is impregnated, dried and reduced in a $\text{H}_2$ stream).	Holzverkohlung Ind. A.-G.: E.P. 305,198, March 27, 1929.
Hydration of ethyl ether; 40% converted into acetone, 10% into ethyl alcohol, and 18% into ethylene.	Hydroxide ppt. from 100 g. Al + 100 g. finely dispersed iron oxide (filtered and dried at $120$ – $130^\circ$ ).	12 g. $\text{MgO}$ .	Kagan, Kossinskaja and Tschernizow: <i>Zhur. Obshchei Khim.</i> , <b>3</b> , 337–344 (1933).
Conversion of mercaptans into thioethers ( $300^\circ$ ).	Sulfides of Fe and Mn; also CdS and ZnS (2–10%).	Difficultly melting carrier such as $\text{MgO}$ , asbestos, or $\text{Al}_2\text{O}_3$ , also active coal.	Standard Oil Development Co. (Frolich): U.S.P. 2,035,121, March 24, 1936.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{V}_2\text{O}_5$ .	$\text{MnO}_2$ or asbestos, infusorial earth, glass, porcelain or quartz.	Chermadarjan and Brodowitsch: <i>Zhur. Priklad. Khim.</i> , <b>7</b> , 725–728 (1934).
Oxidation of CO.	Catalysts, adsorption compounds (3 stages of activity in the life of a catalyst; second stage important).	$\text{MnO}_2$ .	Mathieu-Levy and Gelo: <i>Bull. Soc. Chim.</i> (4), <b>53</b> , 1039–1050 (1933).
Oxidation of $\text{SO}_2$ : $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ .	Pt.	Solid salts such as $\text{CuO}$ , $\text{Fe}_2\text{O}_3$ , $\text{Cr}_2\text{O}_3$ , or $\text{CuO} + \text{Cr}_2\text{O}_3$ .	Grillo and Schroeder: G.P. 102,244 (1898).

Table 41 (Continued).

Reaction	Catalyst	Carrier	Observer
Oxidation of $\text{SO}_2$ : $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$	Pt.	$\text{Fe}_2\text{O}_3 \cdot \text{CuO}$ .	Badische Anilin u. Soda Fabrik; G.P. 291,792 (1913); Swiss P. 71,326 (1913).
Oxidation of: (1) $\text{SO}_2 + 1/2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ . (2) $\text{H}_2\text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$ .	V.	$\text{K}_2\text{O}$ , $\text{VO}_3$ , $\text{SiO}_2$ .	Metall A.-G.: (Siecke and Koolmann); G.P. 610,448, Kl 12, March 13, 1935; G.P. 610,449, Kl 12, March 11, 1935.
Cracking and hydrogenation of oils.	Hydrides of As, Sb, Bi, B, Sn or Si, or halide cmpds. such as $\text{BBr}_3$ (ppt. in the absence of $\text{O}_2$ ); $\text{ZnO}$ or $\text{MgO}$ used in pressure hydrogenation.	Metal oxides such as $\text{CaO}$ , $\text{BaO}$ , or active charcoal, asbestos or graphite.	I. G. Farbenindustrie A.-G. (Mittasch and Zorn); U.S.P. 1,895,764, January 31, 1933.
Preparation of a contact mass.	Ni, Fe, Co and Cu oxides.	Crystalline Al alkalis, borates, or carbonates.	The Barrett Co.; Swiss P. 94,218, April 17, 1922.
Synthesis of $\text{NH}_3$ .	Inert oxides ( $\text{Al}_2\text{O}_3$ , $\text{MgO}$ , $\text{CaO}$ ) and a metal such as Pb, Cd, Bi, Zn.	Nitrate or an amide of a metal (Li).	Urfer: E.P. 199,032, August 9, 1923.
Synthesis of $\text{NH}_3$ .	Fe, Os.	Uranium containing N: $\text{UN}_x + \text{N}_2 \rightarrow \text{UN}_{(x+y)}$ .	Frankenburger: <i>Z. Elek.</i> , 39, 818-820 (1933).

Table 42. Metals and Their Alloys as Carriers.

Reaction	Catalyst	Carrier	Observer
Synthesis of $\text{NH}_3$ .	Fe-Mo-W (evaporation and precipitation on cooled surfaces with simultaneous application of a vapor-like stabilizing agent likewise precipitated).	Wire gauze of Mo, W or Pt.	I. G. Farbenindustrie A.-G.: F.P. 694,076, November 28, 1930.
Catalytic reactions.	Ni (surface origin); converted into Ni carbonyl by passing over $\text{CO}$ ; as catalyst, may serve also as material different from the carrier.	Cu or Ni sheets amalgamated and Hg removed by vacuum distillation.	Catalyst Research Corp. (Bennett and Frazer); U.S.P. 1,940,934, December 26, 1933.
Oxidation of carbon and sulfur oxides.	Alloy containing Cu, Fe, and Mn.	Porous, spongy mass of metals constituting the base portion of the alloy.	Barker: U.S.P. 1,916,249, July 4, 1933.
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ .	Cathodic dispersion of Pt or a layer of Pt.	Fe surface.	Dankow, Joffe and Kotschekow: <i>Khim. Zhur. S.S.S.R.</i> , 4, 334-342 (1933).
Oxidation of $\text{SO}_2$ .	Pt (0.015-0.02%).	Al wire (2 mm. in diam., 3 mm. long), as well as Cr or Ni.	Adadurow, Zeitlin and Orlowa: <i>Ukrain. Khim. Zhur.</i> , 10, 346-361 (1935).
Oxidation of $\text{NH}_3$ .	Pt (5-6%) electroplated.	Ni wire net.	Adadurow and Proserowski: <i>Zhur. Priklad. Khim.</i> , 8, 1321-1329 (1935).
Oxidation of $\text{CH}_3\text{COOH}$ to $(\text{CH}_3)_2\text{CO}$ at 300-400°.	Oxides or hydroxides.	Melted Al, Ca, or Ba stirred to solidification.	Stockholm Superfosfat Fabriks Aktiebolag; E.P. 171,391, December 31, 1921.
Oxidation of alcohols to aldehydes.	Acetic acid.	Cu gauze.	U.S.P. 1,375,345, April 19, 1921.

Table 42 (Continued).

Reaction	Catalyst	Carrier	Observer
Oxidation of $\text{CH}_3\text{COOH}$ to $\text{HCHO}$ ; 92% yield.	Ag (plated).	Cu wire net.	Gurewitsch and Tschirwinskaja: <i>Zhur. Khim. Prom.</i> , 12, No. 1, 57-61 (1935).
Cracking hydrocarbon oils.	Ti, Zr, Th, B, Si.	Fe or not highly alloyed steel.	I. G. Farbenindustrie A.-G.: G.P. 578,504, Kl 23b, June 14, 1933.
Hydrogenation of ethylene.	Pt (plated).	Wire.	Tauber: <i>Z. phys. Chem. (B)</i> , 19, 97-101 (1932).
Hydrogenation and dehydrogenation of organic compounds at 295-300°.	Pd (electrolytically precipitated from Pd chloride solution in dilute $\text{H}_2\text{SO}_4$ at 5-15 milli amp)	Pd wire gauze.	Dow Chemical Co. (Bass): U.S.P. 1,907,710, May 9, 1933.
Hydrogenation of hydrocarbons of all types (hydrogenation of tars, mineral oils, benzoic hydrocarbons, naphthalene, anthracene).	Ni hydrate (paste) containing nitrates of Ag, V, Co, Cd, or their alloys.	Metal spirals, wires, or gauze rolls (catalyst-carrier treated at 240-280° for 40-60 hours before application and reduced with dry $\text{H}_2$ ).	Soc. Ind. des Carburant et Solvant: F.P. 792,507, January 4, 1936.
Hydrogenation and dehydrogenation.	Electrolytically oxidized; density of current less than 0.05 amp./sq. in. (0.008 amp. per cm. <sup>2</sup> ) of the external surface.	Ni or Cu in the form of wires, filings.	Technical Research Works, Ltd.: Austrian P. 17,712, January 3, 1935.
Catalytic reactions.	Porous layer of $\text{NiCl}_2$ obtained on the carrier by treating it at 150° in a stream of chlorine; only the external layer is converted into the chloride; at the same temperature, it is treated with $\text{NH}_3$ gas; $\text{NH}_4\text{Cl}$ formed, volatilizes and escapes; the metal chloride which is converted into a porous, sponge-like metal sticks to the unchanged nucleus of the Ni wire.	Ni wire (2 mm.) (unchanged nucleus).	Soc. d'Étude et d'Exploitation des Matières Organiques: E.P. 350,451, July 20, 1931.

Table 43. Fireproof Material as a Carrier.

Reaction	Catalyst	Carrier	Observer
Oxidation of $\text{NH}_3$ to $\text{NO}$ .	Pt contact mass or Pt alloys.	Grainy sub-layer of fireproof material, oxidized Mg.	Badische Anilin u. Soda Fabrik: G.P. 334,995, Kl 12i, March 18, 1921.
Oxidation of $\text{CH}_4$ : $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$	Ni and Cu.	Fireproof material.	Tessig du Motay: U.S.P. 229,338 (1879). Mond and Langer: G.P. 51,572 (1889).
Incomplete oxidation of $\text{CH}_4$ with $\text{O}_2$ or air at 850-950°; residue gas contains less than 1% $\text{CH}_4$ .	$\text{Ni}(\text{NO}_3)_2$ (impregnated).	Fireproof material.	Padovani and Franchetti: <i>J. Chim. Ind. App.</i> , 15, 429-432 (1933).
Catalytic combustion.		Fireproof clay (500°C.).	Bone and Forshaw: <i>Proc. Roy. Soc. London (A)</i> , 114, 169-180 (1926).
Catalytic heat production.	Pt.	Fireproof earth such as pumice or glass wool.	Gas et Chaleur: F.P. 770,005, September 6, 1934.

Table 44.

Carrier	Catalyst
Carbonaceous materials.	<p>Elements: Pd, Ag, (Zn + Cd), Cu, Al, V, 2A Steel, Fe, Cr, Ni, Pt, Au, W.</p> <p>Oxides: (Fe<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub>), Fe<sub>2</sub>O<sub>3</sub>, ZnO, MnO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, CuO, (CuO + WO<sub>3</sub>), Al<sub>2</sub>O<sub>3</sub>, ThO<sub>2</sub>, Ni + ThO<sub>2</sub>, MoO<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, TiO<sub>2</sub>, H<sub>2</sub>MoO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, Rh colloid, Pt solution.</p> <p>Chlorides: CaCl<sub>2</sub>, ZnCl<sub>2</sub>, NH<sub>4</sub>Cl, PbCl<sub>2</sub>, FeCl<sub>3</sub>, SbCl<sub>3</sub>, SnCl<sub>4</sub>, CuCl<sub>2</sub>, AlCl<sub>3</sub>.</p> <p>Halides: NH<sub>4</sub>Br, NH<sub>4</sub>I, HF, (Mo, U, V) halides, (Ag, Cu, Ni, Sn, Mn, Ni, Co) iodides, (P, S, Se, As, Sb) halides, (Cu, Ag, Zn, Cd, Pb, Sn, Ti, Si, V, Bi, Mo, W, U, Mn, Co, Ni, Fe) halides.</p> <p>Sulfates: 70% H<sub>2</sub>SO<sub>4</sub> + Ag<sub>2</sub>SO<sub>4</sub>.</p> <p>Sulfides: MoS<sub>2</sub>, MoO<sub>3</sub>(NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub>.</p> <p>Acetates: Zn, Mn.</p> <p>Carbonates: Na<sub>2</sub>CO<sub>3</sub>.</p> <p>Carbonyls: Ni.</p> <p>Molybdates: (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>, Al, NH<sub>3</sub>, or Pb(NO<sub>3</sub>)<sub>2</sub> + H<sub>3</sub>PO<sub>4</sub>.</p> <p>Aluminates: Na.</p> <p>Oxalates: Sn or H<sub>2</sub>MoO<sub>4</sub>.</p> <p>Tungstates: NH<sub>3</sub>.</p>
Carbonaceous materials used in catalytic reactions: synthetic, decomposition, reduction, <i>hydrogenation</i> , destructive hydrogenation, <i>pressure hydrogenation</i> , hydration, dehydration, dehydrogenation, desulfurization, chlorination.	

Table 45.

Carrier	Catalyst
<p>Silicates: Silica gel, SiO<sub>2</sub> and Si(OH)<sub>4</sub>.</p> <p>Silica gel is used in catalytic reactions: synthesis, <i>oxidation</i>, reduction, <i>hydrogenation</i>, nitrogenation, chlorination, <i>polymerization</i> and <i>dehydration</i>.</p> <p>Silicates: Silica carbide; Cr, V, or B silicates; Celite sticks; Al silicate; Siloxen (oxydisilin).</p> <p>Silicates used in catalytic reactions: <i>oxidation</i>, reduction, decomposition.</p> <p>Zeolites: Natural, artificial, and polyzeolites.</p> <p>Zeolites used in catalytic reactions: <i>oxidation</i>, reduction, hydrogenation, synthesis.</p>	<p>Elements: Pt, Cu, Ag, Au, Pd, Th, Os, Fe, Co, Ni; colloidal Pt, Pt-Rh, Pd-Pt sponge.</p> <p>Oxides: NiO, WO<sub>3</sub>, TiO<sub>2</sub>, ThO<sub>2</sub>, ZnO, Al<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub> + AlPO<sub>4</sub>, MoO<sub>3</sub>, NO<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>7</sub>.</p> <p>Halides: HCl, HI, HBr, CH<sub>3</sub>Cl, CCl<sub>4</sub>, NH<sub>4</sub>Cl, or NH<sub>4</sub>I; halides of Mo, U, V, or iodides of Ag, Cu, Ti, Sn, Mn, Ni, Co, AlBr<sub>3</sub>, ZnCl<sub>2</sub>.</p> <p>Nitrates: Ni(NO<sub>3</sub>)<sub>2</sub> + Fe(NO<sub>3</sub>)<sub>2</sub> + Al(NO<sub>3</sub>)<sub>3</sub>, or K<sub>2</sub>CO<sub>3</sub>(10n).</p> <p>Vanadates: NH<sub>4</sub>VO<sub>3</sub>, KVO<sub>3</sub> and other vanadium salts.</p> <p>Elements: Ni, Co, Fe, Pt, Os, alkali metals, Cr (steel).</p> <p>Hydroxides: Al(OH)<sub>3</sub>.</p> <p>Acetates: Ni.</p> <p>Chlorides: HCl-Co.</p> <p>Elements: Pt, V.</p> <p>Oxides: V<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub>, NO<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, WO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>7</sub>, Bi<sub>2</sub>O<sub>3</sub>, FeO, CoO, NiO, CuO, Ag<sub>2</sub>O.</p> <p>Chlorides: Pt, W.</p> <p>Vanadates: K, Cu, or Ni.</p> <p>Arsenates: K.</p> <p>Ruthenates: K.</p> <p>Molybdates: NH<sub>3</sub>.</p>

Table 46.

Carrier	Catalyst
Pumice.	<p>Elements: Ni+10% Th, Ag, Ni-Pd, Ni.</p> <p>Oxides: NiO, CoO, CuO, ZnO, (Fe<sub>2</sub>O<sub>3</sub>+Cr<sub>2</sub>O<sub>3</sub>), Cr<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>SiO<sub>3</sub>, MgO, V<sub>2</sub>O<sub>5</sub>, H<sub>2</sub>VO<sub>4</sub>, Co : Cu : MgO (3 : 1 : 0.45), WO<sub>3</sub>, CeO, ThO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>.</p> <p>Chlorides: HCl, CH<sub>3</sub>Cl, CCl<sub>4</sub>, NH<sub>4</sub>Cl, CuCl<sub>2</sub>+1% CeCl<sub>3</sub>.</p> <p>Halides: HI, HBr; halides of Mo, U, V; iodides of Ag, Cu, Ti, Sn, Mn, Ni and Co; ZnBr<sub>2</sub>.</p> <p>Phosphates: H<sub>3</sub>PO<sub>4</sub>, Sn phosphate, Cu phosphate, 90% H<sub>3</sub>PO<sub>4</sub>+ Br<sub>2</sub>, sirupy H<sub>3</sub>PO<sub>4</sub>.</p> <p>Sulfides: CdS, ZnS.</p> <p>Sulfates: H<sub>2</sub>SO<sub>4</sub> (conc.).</p>
Pumice used in catalytic reactions: <i>synthesis</i> , decomposition, <i>oxidation</i> , reduc- tion, hydrogenation, condensation, chlo- rination, dehydration, dehydrogenation.	
Asbestos.	<p>Elements: Pt, Pd, Os, Ni, Ag, Cu, Co, Au, W.</p> <p>Oxides: Fe<sub>2</sub>O<sub>3</sub>+Cr<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, TaO<sub>2</sub>, ThO<sub>2</sub>, TeO<sub>2</sub>.</p> <p>Chlorides: CCl<sub>4</sub>, CHCl<sub>3</sub>.</p> <p>Sulfates: (Cr, Mn, Al, Ca, Ba, Sr, Mg, Ag) sulfates; Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, CaO, BaO, SnO.</p> <p>Nitrates: AgNO<sub>3</sub>; (Ni, Cu, Co, Fe) nitrates.</p> <p>Vanadates: Fe.</p> <p>Oxalates: Ni.</p>
Asbestos used in catalytic reactions: <i>oxidation</i> , <i>reduction</i> , <i>hydrogenation</i> , <i>dehydro-</i> <i>genation</i> , condensation, and dehydration.	

Table 47.

Carrier	Catalyst
Earths: Diatomaceous, Fuller's, infusorial, Florida, puzzolana.	<p>Elements: Pt, Cr, Ni, Fe, Sr, alloys of the 8th Group, Pd-Pt sponge, U, Mn, Ce, Mo, W, Cr.</p> <p>Oxides: Ti<sub>2</sub>O<sub>3</sub> : Ag<sub>2</sub>O : V<sub>2</sub>O<sub>5</sub> (1/4 : 1 : 1), NiO, Fe<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub>, CuO.</p> <p>Chlorides: MgCl<sub>2</sub>, AlCl<sub>3</sub>, CuCl<sub>2</sub>, HgCl<sub>2</sub>, FeCl<sub>3</sub>.</p> <p>Bromides: AlBr<sub>3</sub>.</p> <p>Phosphoric acid: 30% H<sub>3</sub>PO<sub>4</sub>, 80% H<sub>3</sub>PO<sub>4</sub>, 50% H<sub>3</sub>PO<sub>4</sub>, solid H<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>PO<sub>3</sub> : P<sub>2</sub>O<sub>5</sub> (1 : 1).</p>
Earths used in catalytic reactions: <i>oxidation</i> , <i>cracking</i> , pressure hydrogena- tion, <i>polymerisation</i> , chlorination, dehy- dration, desulfurization.	
Kieselguhr.	<p>Elements: Pd, Ni, Co-Th, V, Mo, Zn, Pb, Ag, Sb, Fe-Cu, Cu, Ag-Cd, Co.</p> <p>Oxides: Ti<sub>2</sub>O<sub>3</sub> : Ag<sub>2</sub>O : V<sub>2</sub>O<sub>5</sub> (1/4 : 1 : 1), Al<sub>2</sub>O<sub>3</sub>, MgO, Cr<sub>2</sub>O<sub>3</sub>, ZnO, H<sub>2</sub>SiO<sub>4</sub>.</p> <p>Hydroxides: Zn, Cu, Ag, Cd.</p> <p>Nitrates: (Cu(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>, Ag(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub> activated by chlorides or sulfides, (Ag, Cu, Fe); NaK or NaK<sub>2</sub>.</p> <p>Salts of volatile organic acids.</p>
Kieselguhr used in catalytic reactions: <i>oxidation</i> , <i>synthesis</i> , decomposition, re- duction, <i>hydrogenation</i> and dehydrogena- tion.	
Chamotte.	<p>Elements: Cu, Ni, Fe, Co, Pt (melted together).</p> <p>Vanadates: Ag.</p> <p>Formates: Ni.</p> <p>Butyrates: Mn.</p> <p>Nitrates: Ni.</p>
Chamotte used in catalytic reactions: <i>oxidation</i> and <i>hydrogenation</i> .	

Table 48.

Carrier	Catalyst
Alumina.	Elements: Ni, Th, Ni-Pd. Oxides: CuO, MoO <sub>3</sub> (1.8%) + Cu formate (15%). Phosphates: H <sub>3</sub> PO <sub>4</sub> (90%) + Br <sub>2</sub> . Sulfates: CuSO <sub>4</sub> .
Alumina used in catalytic reactions: <i>dehydration</i> , hydrogenation and <i>dehydrogenation</i> .	
Bauxite.	Elements: Fe, Ni, Co (alone or in a mixture). Oxides: ThO <sub>2</sub> , ZrO <sub>2</sub> , (Fe, Ni, Co + Al <sub>2</sub> O <sub>3</sub> ) containing one or more of the following elements Si, H, C, B, P; CuO, Fe <sub>2</sub> O <sub>3</sub> . Chlorides: MgCl <sub>2</sub> , AlCl <sub>3</sub> , ZnCl <sub>2</sub> . Sulfates: NaHSO <sub>4</sub> , (NaOH + Zn or Al dust). Phosphates: Na <sub>2</sub> PO <sub>3</sub> .
Bauxite used in catalytic reactions: <i>preparation</i> of H <sub>2</sub> (by decomposition and synthesis), dehydration, pressure hydro- genation.	
Kaolin:	Elements: Fe, Ni, Co. Oxides: WO <sub>3</sub> , ThO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , (Fe, Ni, Co + Al <sub>2</sub> O <sub>3</sub> ) containing one or more of the following elements Si, H, C, B; CeO <sub>2</sub> , TiO <sub>2</sub> , Fe <sub>2</sub> O <sub>3</sub> . Sulfates: H <sub>2</sub> SO <sub>4</sub> .
Kaolin used in catalytic reactions: <i>decomposition</i> and dehydration.	
Clay:	Elements: Ni, Cu, Ag. Oxides: CuO, (CuO + Ag <sub>2</sub> O), Cr <sub>2</sub> O <sub>3</sub> , MnO, (NiO + NH <sub>4</sub> ). Chlorides: CuCl <sub>2</sub> , HgCl <sub>2</sub> , CoCl <sub>2</sub> , (CdCl <sub>2</sub> + CuCl <sub>2</sub> ). Hydroxides: Ni(OH) <sub>2</sub> . Sulfates: Hg. Sulfides: Zn. Selenides.
Glassy clay, white acid clay, Japanese acid clay.	
Clay used in catalytic reactions: dehydration, hydrogenation of oils, con- densation, desulfurization.	

Table 49.

Carrier	Catalyst
Porous ceramics.	Elements: Pt, Th, V, 2A steel, Pd, Rh, (Ni + Cr) alloy, 20% and 24%. Oxides: Higher oxides of Mo; V + Al <sub>2</sub> O <sub>3</sub> . Nitrates: AgNO <sub>3</sub> . Cyanides: Fe cyanide; Fe-containing substances. Phosphates: Phosphor-containing; 50% H <sub>3</sub> PO <sub>4</sub> .
Porous ceramics used in catalytic reactions: <i>oxidation</i> , dehydration, hydrogenation.	
Glass:	Elements: Pt, Cu. Oxides: V <sub>2</sub> O <sub>5</sub> , Fe <sub>2</sub> O <sub>3</sub> , CoO, NiO, CuO, Al <sub>2</sub> O <sub>3</sub> . Salts: Mn, (Ni + Mg) or Al, CuSO <sub>4</sub> , NiCO <sub>3</sub> , or Cu mixed with (Ni + Al) cmpds.
Liquid glass, water glass, glass wool, water glass + pumice (paste).	
Glass used in catalytic reactions: <i>oxidation</i> , <i>hydrogenation</i> .	
Quartz:	Elements: Pt, Co, Ni, Cu. Oxides: CuO, Fe <sub>2</sub> O <sub>3</sub> + Cr <sub>2</sub> O <sub>3</sub> , Ce <sub>2</sub> O <sub>3</sub> , Cr <sub>2</sub> O <sub>3</sub> .
Monazite, sand.	
Quartz used in catalytic reactions: <i>oxidation</i> and hydrogenation.	
Cements:	Elements: Fe, Co, Ni. Oxides: Fe <sub>2</sub> O <sub>3</sub> . Hydroxides: Fe(OH) <sub>3</sub> + Na <sub>2</sub> CO <sub>3</sub> .
Gypsum, Portland cement, clinker, etc.	
Cements used in catalytic reactions: <i>oxidation</i> and hydrogenation.	



Table 50.

Carrier	Catalyst
<b>Metals:</b>	<b>Elements:</b> Pt, Ag, Ti, Zr, Th, B, Si, Pd, (Fe-Al) alloy.
	<b>Oxides:</b> Oxides of metals.
<b>Metals, as carriers, used in catalytic reactions: oxidation, hydrogenation, splitting of hydrocarbon oils.</b>	<b>Hydroxides:</b> Hydroxides of metals.
<b>MgO.</b>	<b>Elements:</b>
<b>MgO, as carrier, in catalytic reactions: oxidation, decomposition of solid fats, hydrogenation and hydration.</b>	Pt, Ni, Fe, Co, Cu, Pd, Ir, Ag, Au, Ru, Rh.
	<b>Oxides:</b> NiO, Ni + Al <sub>2</sub> O <sub>3</sub> , (Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> ), Fe <sub>2</sub> CO <sub>3</sub> + K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (0.7%).
<b>MnO<sub>2</sub>.</b>	<b>Oxides:</b> V <sub>2</sub> O <sub>5</sub> , MnO <sub>2</sub> (free from Fe).
<b>MnO<sub>2</sub>, as carrier, used in oxidation reactions.</b>	<b>Adsorption compounds:</b>
<b>Various salts:</b>	<b>Elements:</b> Pt, V, Pb, Cd, Bi, Zn, Fe, Os.
	<b>Hydrides:</b> As, Sb, Bi, B, Sn, or Si.
	<b>Halides:</b> BBr <sub>4</sub> .
<b>Salts, as carriers, in catalytic reactions: oxidation, synthesis.</b>	<b>Oxides:</b> Ni, Fe, Co and Cu; Al <sub>2</sub> O <sub>3</sub> , MgO, CaO.

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# Chapter 8

## Catalytic Reactions in Inorganic and Organic Chemistry

### PART I

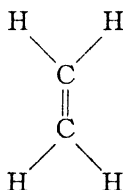
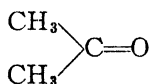
#### How a Catalyst May Control a Chemical Reaction

A catalyst may control a chemical reaction (1) by increasing the reactivity between molecules brought into play in the reaction, and (2) by facilitating the interaction between the reacting molecules by loosening certain linkages or bonds within them. The random introduction of energy into molecules may result in activation at various points; the effect of a catalyst is the loosening of definite linkages so that a combination or an insertion of molecular fragments may take place at favorable points, thus yielding the desired products. It has been learned already from the preceding chapters that under the influence of atomic fields of the catalyst an oriented adsorption may take place and result in the formation of temporary attachment or adsorption complexes between the catalyst and the reacting molecules. These complexes are supposed to be converted readily into reaction products, requiring for this a small activation energy.

Perhaps the first step in the controlling action of a positive catalyst consists in loosening certain linkages and in stabilizing others, whereas a negative catalyst would form an attachment complex with a reacting molecule in which the linkage instead of being loosened, is stabilized. Whether a catalyst actually assists in disrupting certain bonds in reacting molecules for the purpose of producing a better and faster interaction may be learned by considering closely the types of linkages involved and the possible mechanism by which their rupture may be brought about.

The course of a reaction may be traced back to the electrical properties of the molecules and the electronic structure of their component atoms. Lewis<sup>23</sup> in 1916 demonstrated the existence of two types of linkage between two univalent atoms; these were later distinguished by Langmuir<sup>16</sup> in 1919 as (1) the covalence (as in  $\text{Cl}-\text{Cl}$ ) and (2) the electrovalence (as in  $\overset{+}{\text{K}}-\overset{-}{\text{Cl}}$ ). It became clear that a bond can be disrupted in two ways, either of which gives rise to two neutral radicals or to two oppositely charged ions. Numerous reactions are brought about by ionic catalysts, and in many cases these are due to ionization of covalent bonds. In inorganic chemistry, electron transfer leads to the union of elements of opposite type; but in the construction of carbon chains and rings which occurs in organic chemistry, the binding is accomplished by the sharing of electrons between atoms of like elements. Lewis called two shared electrons a "duplet," and

identified it with the bond between atoms. In case of a double bond three possibilities were considered available: (1) double covalence (acetone, ethylene):



(2) double electrovalence:  $\overset{+}{\text{Ca}}\overset{--}{\text{S}}$ , and (3) one covalence and one electrovalence:  $\overset{+}{\text{X}}-\overset{-}{\text{Y}}$ . It was postulated that a double bond in organic chemistry usually reacts as if it contained one covalence and one electrovalence.<sup>26</sup>

To stress the fundamental difference existing between covalent and electrovalent linkages their characteristics were considered separately. It was recognized that: (1) in covalent compounds linking electrons or linking orbits form part of the electronic constitution of both atoms concerned in the bond formation; (2) in covalent compounds the positions of atoms in space relative to the linking orbits is fixed and cannot be altered without causing the rupture of linkages; (3) stereoisomerism is a property of covalent (homopolar) linkages, and this explains their occurrence in carbon chemistry. Covalences possess definite directions in space and the same sets of atomic nuclei are capable of several arrangements around a particular atom; (4) covalence implies neutralization and the electrical forces in a covalent compound are more or less compensated within the molecule; (5) the work required to separate molecules of ionized compounds is greater than in the case of covalent compounds.

In electrovalent compounds there is (1) no real bond between the oppositely charged ions; they are strongly attracted to one another by electrostatic forces and are free to take up any relative positions; (2) the ions of electrovalent compounds take up a position determined by forces of attraction under given conditions, and therefore only one arrangement in space is possible, excluding the occurrence of stereoisomerism; (3) electrovalent compounds are made up of ions, and as a result strong fields of electrical forces exist outside of the molecule. The process of neutralization occurs by a so-called "head and tail" arrangement. The positive electrical field surrounding a cation in an electrovalent molecule is responsible for neutralization of the negative electricity surrounding the anion of another molecule.

The transition of one form of valence linkage into the other was developed by Fajans<sup>7,8</sup> who assumed that ions are not rigid, unalterable structures but exert a definite deforming effect on each other in the crystal lattices of electrovalent molecules. According to Fajans, when two oppositely charged ions approach each other the deformation they produce on each other will at a certain point cause these electrons to divert into new orbits containing both atoms, whereby a covalent linkage will be formed.

Fajans emphasized that the tendency toward such transformation depends on the attraction of the cation for electrons and on the firmness with which the anion holds on to its electrons. When the cation is small and the anion large and the valence or charge high, favorable conditions are provided for the promotion of deformation, leading to the conversion of electrovalence into covalence. On the contrary, a large cation, a small anion, and a low charge assist deformation, leading to the formation of polar, electrovalent compounds.

With regard to properties, a normal covalence must be differentiated from a co-ordinate covalence, or so-called semi-polar double bond. The difference is due to the fact that in the second case atom *B* receives a share of two electrons originally belonging to atom *A*. In other words the co-ordinate linkage is accompanied by segregation of positive and negative electricity, which is termed polarization. The co-ordinate valence produced by a process of unequal sharing of electrons corresponds to a process of intramolecular ionization manifested in the production of a high dielectric constant of the compound. A co-ordinate covalence is usually more readily ruptured than a normal covalence.

One of the chief characteristics of an electrovalent molecule is the possession of an electrical dipole moment  $\mu$ , as emphasized by Lewis. The dipole moment may be expressed as the product of charge  $e$  on either of the ions concerned and the distance  $d$  between their atomic centers. A covalent molecule has a zero dipole moment if its electrons are arranged symmetrically around the nuclei (*e.g.*, the electrical center of all electrons and the center of positive nuclei coincide). Any deviation from this will produce an electrical dipole which gives rise to a definite electric moment.

The most obvious property of a dipole is its tendency to rotate, in order to set itself in the direction of lines of force of an electrostatic field, similar to the orientation of a magnet in a magnetic field. A molecule with a large dipole moment produces a relatively strong field of force around the molecule, and these stray fields are considered largely responsible for the van der Waals' forces.<sup>22</sup> Not only have the different types of linkage been established, but also the methods for distinguishing between electrovalent and covalent molecules. Measurements have likewise been provided for establishing the presence of semi-polar double bonds and for ascertaining the magnitude of the dipole moments of compounds.

Compounds containing the co-ordinate linkage are intermediate in volatility between those which have only normal covalent and electrovalent bonds. The major factors to be used for differentiating between electrovalent and covalent molecules are: (a) conductivity (for compounds soluble in water); (b) presence or absence of stereoisomerism; (c) degree of volatility (electrovalent molecules require work in their separation, and their liquids boil at much higher temperature than those of covalent compounds); (d) solubility in hydrocarbon solvents, *e.g.*, petroleum or benzene (inorganic salts insoluble, organic compounds soluble); (e) the type of packing (x-ray analysis of crystals). Ionized salts assume a close-packed form, while covalent molecules adopt an open structure in the crystalline

state (MgO and CaO are electrovalent with close-packed structure, BeO and CaS are covalent, with an open structure).

It has been suggested by Sugden and co-workers<sup>38, 39, 40</sup> that the presence of semi-polar double bonds in molecules may be established either by determining Sugden's "parachor" or by measuring polarization. The type of mixed valence Sugden<sup>37</sup> expressed by the symbol  $+ -$ . The parachor value is obtained from the following formula:

$$(P) = \frac{M(\text{mol. wt.})}{D(\text{density of the liquid phase}) - d(\text{density of the vapor phase})} \times \gamma^{1/4}$$

where  $\gamma$  is the surface tension of the liquid. Sugden's findings indicate that compounds with a lower parachor value are those in which the electronic theory led to the assumption of a mixed or semi-polar bond. The following tables give an estimate of parachor values, both atomic and structural.

Table 1. Atomic Parachors.

C = 4.8	S = 48.2
H = 17.1	F = 25.7
N = 12.5	Cl = 54.3
P = 37.7	Br = 68.0
O = 20.0	I = 91.0

Table 2. Structural Parachors.

Triple bond = 46.6	4-member ring = 11.6
Double bond = 23.2	5-member ring = 8.5
3-member ring = 16.7	6-member ring = 6.1

Table 3. Parachors of Non-polar Double Bonds.

Compound	Formula	Parachors	
		Double Bond	Atomic
Ethylene.	<chem>CH2=CH2</chem>	21.5	78.0
Propylene.	<chem>CH3CH=CH2</chem>	22.9	117.0
Acetone.	<chem>CH3C(=O)CH3</chem>	24.5	137.0
Diethyl ketone.	<chem>C2H5C(=O)C2H5</chem>	21.2	215.0
Carbon disulfide.	<chem>S=C=S</chem>	$21.8 \times 2$	101.2
Ethyl isothiocyanate.	<chem>C2H5N=C=S</chem>	$25.5 \times 2$	160.6
Nitrosyl chloride.	<chem>O=NCI</chem>	21.3	86.8
Nitrosodimethylamine.	<chem>CH3N(=O)CH3</chem>	27.1	157.2

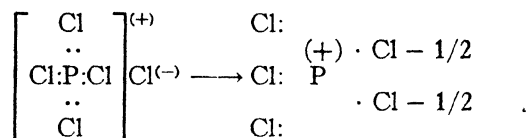
In parachor calculations the duplet or ordinary covalence is taken as zero; in the non-polar double and triple bonds each electron in excess of this adds 11.6 units to the parachor. The parachor of a semi-polar double bond is  $-1.6$  and the parachor of a singlet semi-polar linkage is estimated to be equal to  $-\left(11.6 + \frac{1.6}{2}\right) = -12.4$ .

The single linkage, termed "singlet," is considered to be a somewhat

Table 4. Parachors of Semi-polar Double Bonds.

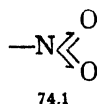
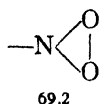
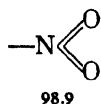
Compound	Formula	Parachors	
		Double Bond	Atomic
Phosphoryl.	$\bar{O}-\overset{+}{P}Cl_3$	-3.0	220.6
Ethyl phosphate.	$\bar{O}-\overset{+}{P}\begin{matrix} \diagup O \cdot C_2H_5 \\ \diagdown O \cdot C_2H_5 \\ \diagdown O \cdot C_2H_5 \end{matrix}$	-3.9	403.0
Diethyl sulfide.	$\bar{O}-\overset{+}{S}\begin{matrix} \diagup O \cdot C_2H_5 \\ \diagdown O \cdot C_2H_5 \end{matrix}$	+1.3	298.4
Diethyl sulfonate.	$\begin{matrix} \bar{O} \\ \bar{O} \end{matrix} \rangle \overset{++}{S} \begin{matrix} \diagup O \cdot C_2H_5 \\ \diagdown O \cdot C_2H_5 \end{matrix}$	$-1.3 \times 2$	295.8
Methyl sulfate.	$\begin{matrix} \bar{O} \\ \bar{O} \end{matrix} \rangle \overset{++}{S} \begin{matrix} \diagup O \cdot CH_3 \\ \diagdown O \cdot CH_3 \end{matrix}$	$-0.75 \times 2$	240.4
Ethyl sulfate.	$\begin{matrix} \bar{O} \\ \bar{O} \end{matrix} \rangle \overset{++}{S} \begin{matrix} \diagup O \cdot C_2H_5 \\ \diagdown O \cdot C_2H_5 \end{matrix}$	$-2.3 \times 2$	318.4
Sulfuryl chloride.	$\begin{matrix} \bar{O} \\ \bar{O} \end{matrix} \rangle \overset{++}{S} \begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix}$	$-1.65 \times 2$	196.8
Average		-1.6	

labile form of a covalence linkage, but actually singlet linkages are semi-polar single bonds. Langmuir,<sup>18</sup> maintaining the octet rule, gives the following polar formula for the labile halogen atoms held by semi-polar single bonds in phosphorus pentachloride.



Sugden, examining co-ordinate compounds, observed that an ordinary double bond gave an increase of 23.2 units in the parachor; a semi-polar double bond gave a small decrease in the parachor, due to electrostatic attraction between the poles and averaging -1.6 units. The values for some of the compounds examined are given in Table 5.

The parachors of nitro- groups are:



and the average value obtained from 13 different compounds containing the nitro- group is 73.0; thus only the third formula is possible.

Compound	P (observed)	P (calculated) for One Semi-polar Double Bond
Azoxybenzene.	444.7	446.6
<i>n</i> -Methyl ether of benzaldoxime.	325.9	321.1



Table 5. Parachors of Co-ordinate Compounds (Sugden).

Compound	<i>P</i> (calculated)	Semi-polar Double Bond
$\text{Cl}_3\text{P}=\text{O}$	220.6	-3.0
$(\text{PhO})_3\text{P}=\text{O}$	687.7	-1.2
$\text{Cl}_2\text{S}=\text{O}$	176.8	-2.3
$\text{Cl}_2\text{S}=\text{O}$	196.8	$-1.65 \times 2$
$\text{MeO}-\text{S}(=\text{O})_2$	240.4	$-0.75 \times 2$
$\text{EtO}-\text{S}(=\text{O})_2$	318.4	$-2.3 \times 2$

The parachor indicates that these compounds contain a semi-polar double bond between nitrogen and oxygen. On the other hand the parachors of nitrosyl chloride and of esters of nitrous acid indicate that these compounds do not contain a co-ordinate link and possess the formula  $\text{X} - \text{N} = \text{O}$ . Likewise the isothiocyano radical in thiocarbimides is non-polar.

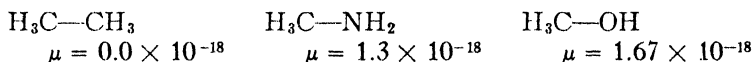
Compound	<i>P</i> (calculated)
Nitrosyl chloride	110.0
<i>n</i> -Butyl nitrite	248.8
Allyl thiocarbimide	235.0
Benzene	206.2

The polarization in a molecule follows from its molecular electric moment, calculated from measurements of the dielectric constant using Debye's method. Two types of polarization are recognized: (1) orientation polarization which is due to the partial alignment of the permanent dipoles in an electric field, and is designated by  $P_\mu$ ; (2) induced polarization which results from the distorting effect of an outside electric field on the constituent part of the molecule. The induced polarization is subdivided into atomic polarization,  $P_A$ , and electronic polarization,  $P_E$ . Atomic polarization is distinguished from electronic polarization in that the former represents the displacement of the heavier part of the atom, the nuclei, away from their equilibrium positions, while the latter represents a similar shift for the lighter portions of the atoms, the electrons. While electronic polarization contributes chiefly to the dielectric constant, atomic polarization provides a measure of the tendency toward dissociation into ions.

The molecular dipole may be determined by a comparison of the dielectric constant in the solid state with that in a dilute solution or gaseous state. Debye determined approximately that if  $\epsilon$ , the dielectric constant, differs from  $n^2$ , or if  $(\epsilon - 1)$  is greater than  $2(n - 1)$  the molecule is polar ( $n$  is the refractive index of the medium). Refractive indices do not often exceed 1.5; thus a dielectric constant greater than 2 would indicate that the molecules are polar.

It has been definitely proved that, in a molecule of ethane in which the electrons of the carbon-to-carbon bond are symmetrically distributed, the dipole moment is zero. By replacing *C* by another atom such as *N* or *O*,

the electrical symmetry is distorted on account of the difference in nuclear charges controlling the electrons in the covalence, and a dipole is produced, the value of which in electrostatic units is given below for methylamine and methyl alcohol:



It has been ascertained that compounds containing semi-polar bonds generally have large permanent dipoles, while smaller dipole moments are associated with covalent bonds between atoms of different atomic numbers. Furthermore, by dissecting the observed dipole moments of a large number of organic compounds Sidgwick<sup>36</sup> gives a table of dipole moments of individual links (in  $10^{-18}$  electrostatic units).

Table 6. Dipole Moments of Individual Links (Sidgwick).

H—C	0.2	C—C	0.00	P—Cl	0.8
H—N	1.5	C—N	0.4	P—Br	0.6
H—O	1.6	C≡N	3.3	As—Cl	2.0
H—S	0.8	C—O	0.9	As—Br	1.7
H—P	0.55	C=O	2.5	Sb—Cl	3.9
H—As	0.15	C≡O	5.3	N=O	1.9
H—F	(2)	C—F	1.5	C—S	1.2
H—Cl	1.03	C—Cl	1.7	C=S	3.0
H—Br	0.78	C—Br	1.6	C—Se	1.1
H—I	0.38	C—I	1.4	C—Te	0.9

Thomson<sup>41</sup> attributed the presence of dipoles to intramolecular ionization, and classified gaseous molecules as: (1) those without dipoles and (2) those in which dipoles are present.

Class 1:  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{Cl}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$

Class 2:  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CHCl}_3$

Dipole moments were often associated with high boiling and high melting points. When all the partial moments are compensated, and the connecting lines between various components of the compound form with one another angles of a regular tetraeder, no dipole moment can be expected.

Saturated aliphatic hydrocarbons (branched and unbranched) have a dipole moment equal to zero. Ethylene and acetylene have no dipole moment. Benzene has no dipole moment (all partial moments compensate one another). If in an aliphatic saturated hydrocarbon one of the hydrogen ions is replaced by a chlorine ion, then the partial moments in the molecule do not compensate any more and the molecule acquires a dipole moment.

Hydrocarbon	Dipole Moment p. $10^{-18}$
$\text{CH}_4$	0
$\text{CH}_3\text{Cl}$	1.9
$\text{CH}_2\text{Cl}_2$	1.6
$\text{CHCl}_3$	1.0
$\text{CCl}_4$	0

Since all C—C bonds in a chain of normal paraffinic hydrocarbons are

of nearly equal strength, it appears that the splitting probability is equal for each bond. This can be calculated from Lorentz' equation:

$$W = \left(1 - \frac{\Sigma}{E}\right)^{3n-1}$$

where  $E$  is the total energy;  $n$ , the quantity of equally heavy groups being held together by nearly equal forces, and  $\Sigma$ , the energy of the bonds between two groups.

However, it has been ascertained by Höjendahl<sup>11</sup> that the above substitution has little effect on the state of other hydrogens, and for all aliphatic monochlor derivatives a dipole moment of almost equal value is obtained.

Table 7. Dipole Moments of Aliphatic Monochlor Derivatives (Højendahl).

CH <sub>3</sub> Cl	1.89	C <sub>4</sub> H <sub>9</sub> Cl	2.16
C <sub>2</sub> H <sub>5</sub> Cl	2.06	CH <sub>2</sub> =CH · CH <sub>2</sub> Cl	1.97
CH <sub>3</sub> CH <sub>2</sub> · CH <sub>2</sub> Cl	2.11	C <sub>6</sub> H <sub>11</sub> CHCl · CH <sub>3</sub>	2.0
CH <sub>3</sub> CHClCH <sub>3</sub>	2.18	C <sub>4</sub> H <sub>9</sub> CHCl · C <sub>2</sub> H <sub>5</sub>	2.1
		C <sub>3</sub> H <sub>7</sub> CHCl · C <sub>3</sub> H <sub>7</sub>	2.0

On the other hand chloroform has not the same dipole moment as methylchloride, as would be the case if the dipole moment in CH<sub>3</sub>Cl were present only, due to the fact that the moment of one of the C—H bonds has been replaced by the moment of the C—Cl bond. Actually, through the introduction of a chlorine the tetraeder has been distorted, the angles which atoms form with one another are changed, and the partial moments of C—H bonds are not necessarily directed exactly toward the central C atom.

The polarization of hydrogen ions increases, as they are less crowded, while the distance from C to H is presumed to be smaller when the hydrogen ions are loosely bound to the corresponding C ion. On account of changes in the molecule the partial moment of the CH<sub>3</sub> group in (CH<sub>3</sub>H) and (CH<sub>3</sub>Cl) will be different. If the CH<sub>3</sub> group in CH<sub>4</sub>, *i.e.*, (CH<sub>3</sub><sup>+</sup>H<sup>-</sup>), is considered as a positive complex built of strongly deformed ions, then this deformation will be due to a displacement of ions within the radical or to the kind of substitute. The deformation of the CH<sub>3</sub> group under these circumstances can be greater through the action of the fourth H ion than in CH<sub>3</sub>Cl. According to Estermann<sup>5</sup> the total dipole moment of CH<sub>3</sub>Cl should be due to the difference between the charge of both ions (CH<sub>3</sub><sup>+</sup> and Cl<sup>-</sup>), that is, the oppositely directed moments of the deformed CH<sub>3</sub> group and the polarized Cl ion.

It has been found that, although for hydrogen halides the moments strongly decrease in the series HCl, HBr, HI, because the induced moment increases faster than the charged moment, in the case of methyl halides the decrease is smaller in the corresponding series, because the moment of the CH<sub>3</sub><sup>+</sup> group also directed opposite to the charge moments decreases with increase of the halide moment. In general the dipole moment of alkyl halides differ little, as shown in Table 8.

Stevels<sup>36a</sup> developed a method by means of which it is possible to calculate the direction of polarization of a definite H atom or halogen atom X, if this passes through a series of methane derivatives. A table shows by which value the refraction of this H or halogen atom is changed through

Table 8. Dipole Moments of Alkyl Halides.

Compound	Dipole Moment p. $10^{-18}$
$\text{CH}_3\text{Cl}$	1.89
$\text{CH}_3\text{Br}$	1.82
$\text{CH}_3\text{I}$	1.66
$\text{C}_2\text{H}_5\text{Cl}$	2.06
$\text{C}_2\text{H}_5\text{Br}$	2.09
$\text{C}_2\text{H}_5\text{I}$	2.00

the presence of other substituents (H or halogen), when compared with the refraction of the compound  $\text{CX}_4$  in the liquid state. This course of the atomic refraction of a definite H or halogen atom in a series of methane derivatives may be compared with the course of dipole moments of similar substances. It is not necessary to assume a repulsion effect between halogen atoms in the compound  $\text{CHX}_3$  in order to explain the difference between the dipole moments of  $\text{CH}_3\text{X}$  and  $\text{CHX}_3$ . The theory is applied to ethane derivatives with 1, 2 and 3 halogen atoms. All regularities taking place thereby may be explained in a simple manner. The magnitude of the dipole moments of the compounds considered appears to be justified, if the number and strength of the bonds of H atoms to the C atom holding the halogen atoms is taken into consideration. The length of the carbon chain has little effect on the dipole moment in a homologous series of straight-chain paraffinic alcohols, the moment residing principally in the C—O—H group.

Compound	Dipole Moment p. $10^{-18}$
$\text{C}_2\text{H}_5\text{OH}$	1.72
$n\text{-C}_3\text{H}_7\text{OH}$	1.65
$n\text{-C}_4\text{H}_9\text{OH}$	1.74
$n\text{-C}_6\text{H}_{11}\text{OH}$	1.66

Sänger and Steiger<sup>33, 34</sup> found the following values for the dipole moment of ethers; the existence of a moment indicates an unsymmetrical structure which, as in the case of water, was assumed to be triangular.

Compound	Dipole Moment p. $10^{-18}$
$\text{H}_2\text{O}$	1.85
$(\text{CH}_3)_2\text{O}$	1.32
$(\text{C}_2\text{H}_5)_2\text{O}$	1.10
$(\text{C}_3\text{H}_7)_2\text{O}$	0.85

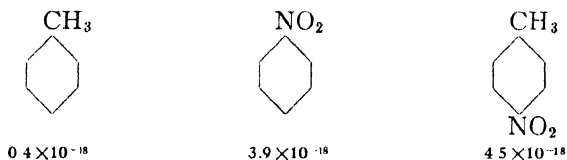
Both saturated aliphatic hydrocarbons and aromatic hydrocarbons, if symmetrical, have zero moment. The dipole moments of phenyl halides are lower than the corresponding alkyl halides. The moments of phenyl halides are as follows:

Compound	Dipole Moment p. $10^{-18}$
$\text{C}_6\text{H}_5\text{Cl}$	1.55
$\text{C}_6\text{H}_5\text{Br}$	1.50
$\text{C}_6\text{H}_5\text{I}$	1.25
$\text{C}_6\text{H}_5\text{F}$	1.39

The moment of phenyl fluoride is smaller than that of phenyl chloride; the moment of  $\text{CH}_3\text{F}$  has not been determined. As a rule, the dipole moments of *ortho* compounds are greatest, and the *para* compounds have no dipole

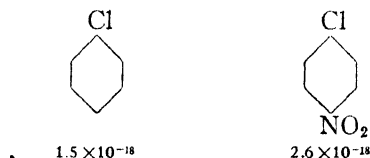
moment. If both substituents are not equal, then the *para* compounds have a dipole moment corresponding to the difference between the two partial moments.

The moments of nitroparaffins were found to be smaller than those of nitrobenzene. The polarization of the methyl group toward the benzene ring is opposite in direction to that of the nitro- group. This fact is established by the moments of corresponding compounds which are:



The moments are of opposite sign because otherwise the resultant dipole moment would be  $3.5 \times 10^{-18}$ .

In the case of chlorobenzene and *p*-nitrobenzene, the dipole moment of C—Cl has the same direction as that of the C—NO<sub>2</sub>, and, since these two moments oppose one another, the overall moment of the molecule is the difference of the two values rather than the same value.



The introduction of a nitro-group into toluene greatly affects the dipole moment: toluene has a dipole moment  $0.4 \times 10^{-18}$ ; *p*-nitrotoluene has a dipole moment  $4.5 \times 10^{-18}$ .

The corresponding values of the dipole moment for other substituents are:

Substituent	Dipole Moment p. $10^{-18}$
NO <sub>2</sub>	-3.9
OH	-1.7
Cl	-1.5
Br	-1.5
I	1.25
COOH	-0.9
NH <sub>2</sub>	-1.5

The C—H bond in hydrocarbons is influenced by the remainder of the molecule; its value in saturated aliphatic compounds is different from those in olefinic or aromatic hydrocarbons. Hydrocarbons in which an aliphatic hydrocarbon group is bound to an aromatic or in which simple and double bonds are present, possess dipole moments of a small order of magnitude, for example:

Toluene (C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )	$p = 0.52 \times 10^{-18}$
Trimethylethylene (CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>3</sub>	$p = 0.47 \times 10^{-18}$
$\alpha$ -Butylene (CH <sub>2</sub> =CH · CH <sub>2</sub> · CH <sub>3</sub> )	$p = 0.37 \times 10^{-18}$

It was found that diphenyl ( $\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_5$ ) has no moment, from which it was deduced that the molecule has the elongated structure, the  $p, p'$ -carbon atoms being on one straight line with the bond connecting the two phenyl groups.  $p, p'$ -Dihalogen derivatives of diphenyl have no moment. If the substituent group is an oxy-alkyl or a hydroxyl, the  $p, p'$  derivative has a moment. Carbon dioxide and carbon disulfide have a zero moment. This shows a linear structure for these molecules. The attachment of the carbon monoxide group to aliphatic or aromatic radicals to form a ketone results in a molecule with a moment of about  $2.74 \times 10^{-18}$ . COS has a dipole moment  $\mu = 0.65 \times 10^{-18}$ .

Two atoms carrying opposite electric charges, *e.g.*, ions are not always bound together by electrostatic forces. Electrostatic binding is possible also between uncharged atoms which are electrically unsymmetrical, *i.e.*, possess a dipole moment through which they may polarize one another. However, in numerous compounds of inorganic and organic chemistry, electrostatic binding cannot be assumed as an explanation. Fajans<sup>9</sup> considered in these cases the existence of an atomic binding equivalent to an ionic binding with extreme polarization. He illustrated his thought by the following scheme:

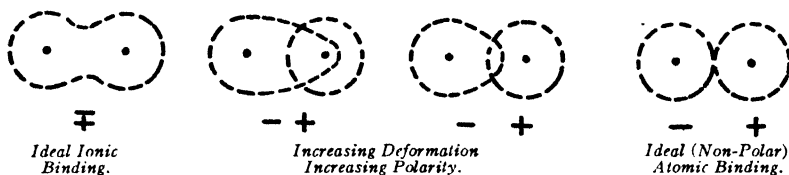


FIGURE 1.—Fajans' Scheme.

Lewis<sup>24</sup> conceived the idea that while many molecules contain permanent electrical dipoles, polarity may be introduced throughout a molecule as well as upon those in its vicinity by a mechanism of "electrostatic induction." A polar group may induce in a bond a dipole in the sense required for chemical activation and thereby increase the reactivity of this bond. Thomson<sup>41</sup> has recognized the possibility of promoting reactions between molecules by creating conditions necessary for the occurrence of intra-molecular ionization. He pointed out that ionic dissociation of a molecule depends on augmenting its dipole moment, and that this is carried out in the case of proximity of molecules either already ionized or possessing strong dipole moments.

Should polar effects influence both the activation of covalent linkages in a molecule and the ease of attack of a compound by the reacting molecules or ions around it in the system, then the function of a catalyst could be described as that of a reagent exerting or inducing polar influences (Berkman).

Sidgwick<sup>36</sup> gives data for dipole moments of substituent groups in the aromatic and aliphatic compounds which prove the fact that dipoles in a molecule may exert a mutual induction upon one another, and that transmission of polarity occurs along a chain of atoms, at least in the case of atoms or radicals, which are most readily polarized. It is stated that when

an ionizable reagent (in our case it would be a catalyst) is added to an olefin, the double bond in the molecule is activated from a covalent to a semi-polar bond, which then reacts with the ions of the reagent. The activation of the double bond and the ionization of the reagent (catalyst) may be considered as effected by general polar influences operating between the molecules involved.

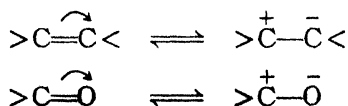
Table 9. Dipole Moments of Substituent Groups (Sidgwick).

Aromatic Series		Aliphatic Series	
Aryl: $-\text{CH}_3$	+0.45	Alkyl: $-\text{CH}_3$	-0.00
$-\text{OCH}_3$	-1.06	$-\text{OCH}_3$	-1.29
$-\text{NH}_2$	+1.55	$-\text{NH}_2$	+1.23
$-\text{Cl}$	-1.56	$-\text{Cl}$	-2.15
$-\text{Br}$	-1.52	$-\text{Br}$	-2.21
$-\text{I}$	-1.27	$-\text{I}$	-2.13
$-\text{CH}_2\text{Cl}$	-1.82	$-\text{CH}_2\text{Cl}$	-2.03
$-\text{CHCl}_2$	-2.03	$-\text{CHCl}_2$	-2.06
$-\text{CCl}_3$	-2.07	$-\text{CCl}_3$	-1.57
$-\text{COCH}_3$	-2.97	$-\text{COCH}_3$	-2.79
$=\text{CO}$	-3.04	$=\text{CO}$	-2.76
$-\text{CN}$	-3.89	$-\text{CN}$	-3.46
$-\text{NO}_2$	-3.93	$-\text{NO}_2$	-3.05

The change in the dipole moment of a bond follows either through the action of an inner molecular electric field or through an association with a dipole. The effect is expressed in a shift of the double bond through electrons, which leads to an increase or decrease in the original moment. With regard to influences deforming the electrostatic field within the molecule, the following have been differentiated: (1) actions of free electric charges and (2) action of the electric field of one upon the other.

It has been also assumed that the polar effect of a radical may be transmitted by a process of electrostatic induction from atom to atom, or from bond to bond, within the molecule. Lapworth<sup>19, 20, 21</sup> postulated that a dipolar radical can polarize an adjacent covalent bond, producing thereby a small secondary dipole, which in its turn can induce electrical polarization in the next bond. He considered the induced polarity as a phenomenon similar to that when a bar magnet induces magnetization in a chain of soft iron filings.

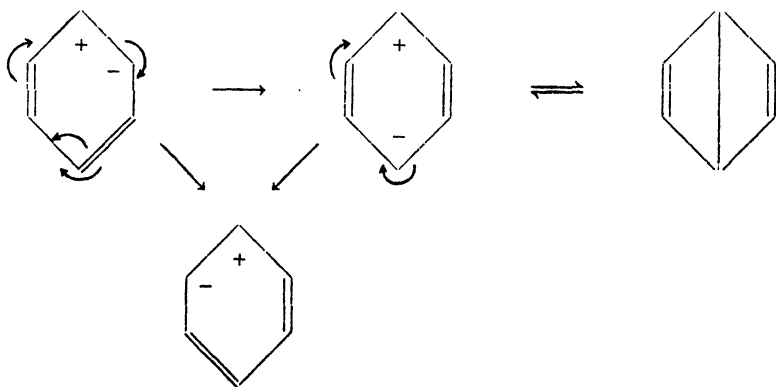
The different behavior of the two principal types of unsaturated compounds has been interpreted in terms of the electronic configuration of atoms forming the double bond and of the unequal affinity which these atoms acquire as a result of polar activation of the double bond. It has been ascertained that in all addition reactions of unsaturated compounds the characteristics displayed are not those of the normal covalent form, but of a semi-polar or activated structure. The readiness in adding to olefins has been regarded as due to the high reactivity of the polar centers in the activated form. The formation of addition products by unsaturated compounds in certain instances may be attributed to a polar activation of the double bond. An ionic reagent gives rise to an unstable semi-polar bond.



In the activation process a pair of shared electrons is transferred from the double bond to the atom of C or O, which acquires a negative unit charge in the activated product.

The characteristic reactions of aldehydes and ketones has been attributed to a polar activation of the carbonyl group  $>\overset{+}{\text{C}}=\overset{-}{\text{O}}$ , namely, to the semi-polar form  $\overset{+}{\text{C}}-\overset{-}{\text{O}}$ . In this process of activation oxygen becomes a negative pole capable of reacting with cations such as  $\text{H}^+$  or with reagents readily yielding reactive cations, while the carbon atom as a positive pole is able to react with anions such as  $\text{CN}^-$ , or with reagents yielding readily active anions. Thus the carbonyl group reacts well with reagents in which the cation is active and the anion inert.

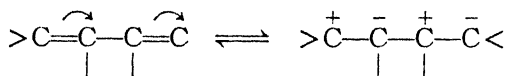
Lapworth<sup>16, 17, 18</sup> applied to aromatic substitution his theory of the relationship of polarity to chemical change; he explained the production of reactivity at particular points in a benzene ring by substituent groups of a polar character. In other words an aromatic compound becomes active through an induced electrical polarity. Lapworth and Robinson assumed that polar activation of an aromatic ring, developed from one double bond, does not spread automatically throughout the whole system, but yields a simple dipole with two charges, both of which may migrate. Ingold<sup>12</sup> believes this migration takes place by electron movement around the ring or the electromeric changes may also occur directly across the benzene ring as illustrated.



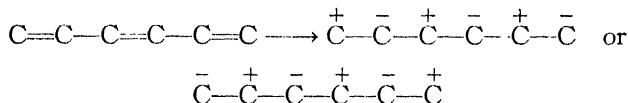
Lowry<sup>26</sup> postulated an electronic interpretation relating to conjugated systems based on the polar activation of covalent bonds. It has been assumed that only activated molecules undergo chemical changes and that the properties of conjugated systems depend on the possibility of ionizing the successive double bonds and recombining the ionic charges between adjacent atoms, so that an electronic charge migrates from end to end of the system. The direction of migration is given by the pressure of electrons at the ends of the system, so that the dipole moment of the substituents determines the course of the chemical charge. Thus, when a conjugated



system enters into combination with an ionic reagent, the activation proceeds as follows:



The characteristic property of a conjugated chain of atoms is therefore its ability to develop a series of alternate positive and negative charges on alternate atoms by activating the double bonds.



Hinshelwood and Glass<sup>10a</sup> found that iodine has a pronounced catalytic effect on the thermal decomposition of isopropyl ether and that the catalytic reaction is homogeneous. A simplified activation mechanism is suggested for the reaction, consisting of the migration of a hydrogen atom and the breaking of a bond which possesses a dipole moment. The polar nature of the bond which is broken and the polarizability of the iodine molecule facilitate the energy transfer to that particular point. The bond is weakened by the action of the catalyst, which is the iodine molecule rather than the iodine atom. The effect of the catalyst amounts to an increase in perturbation factor required by quantum mechanics for energy transfer.

Lapworth,<sup>16, 17, 18</sup> Robinson<sup>30</sup> and Ingold<sup>13</sup> proposed that all reagents of organic chemistry be classified into anionoids (giving off electrons) and cationoids\* (taking up electrons). From this point of view unsaturated

Table 10. Classification of Organic Reagents (Robinson).

Anionoids	Cationoids
(1) Active anions: OH, NH <sub>2</sub> , CN, CH(COOEt) <sub>2</sub> .	(1) Protons and sources of protons, <i>e.g.</i> , acids and pseudo-acids, diazonium ions, cations from pseudo-bases, <i>e.g.</i> , cotarnine.
(2) Reducing agents, including all metals and ions which can give up electrons, <i>e.g.</i> , Na, Mg, Fe, Fe'' and Fe(CN) <sub>5</sub> '''.	(2) Oxidizing agents including the halogens, ozone, peroxides and ions which can accept electrons; CrO <sub>2</sub> -, Fe <sup>+++</sup> , Fe(CN) <sub>5</sub> ---, MnO <sub>4</sub> -.
(3) Alkyl and aryl residues of organo-metallic compounds: Et in EtMg · Br and R · C≡C in RC≡C · Na.	(3) Alkyl residues from esters, <i>e.g.</i> , Me in MeI or Me <sub>2</sub> SO <sub>4</sub> , alkyl residues from quaternary ammonium salts and bases, <i>e.g.</i> , Me from Ph <sub>4</sub> NMe <sub>2</sub> OH.
(4) Donor molecules containing lone pairs of electrons such as NH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> N, H <sub>2</sub> O, Et <sub>2</sub> O, CH <sub>3</sub> COCH <sub>3</sub> (on the oxygen), R · SH, R <sub>2</sub> S.	(4) Acceptor atoms, ions and molecules including metallic atoms and ions capable of coordinating with H <sub>2</sub> O, NH <sub>3</sub> , etc., <i>e.g.</i> , ZnCl <sub>2</sub> , PtCl <sub>4</sub> .
(5) Unsaturated carbon of olefins and aromatic hydrocarbons: C <sub>2</sub> H <sub>4</sub> , C <sub>6</sub> H <sub>6</sub> .	(5) Atoms which carry or easily acquire positive charges, <i>e.g.</i> , in semi-polar bonds: C in >CO; -COOEt, -CN; S in SO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , NaHSO <sub>4</sub> ; N in -NO; -NO <sub>2</sub> , HNO <sub>2</sub> .

hydrocarbons acting by forming a semi-polar bond are classed as "cationoid" if the positive pole is more reactive than the negative pole, and as "anionoid" if on the contrary the negative pole is more reactive than the

\*The original definition of cationoids and anionoids is stated as follows: "If the formation of a covalent bond in the complex A—B takes place by the union of  $\bar{A}$  with  $\bar{B}$  then A is anionoid and B cationoid."<sup>30</sup>

positive one. The olefins yield two very reactive poles:  $>\text{C}=\text{C}< \rightleftharpoons >\overset{+}{\text{C}}-\overset{-}{\text{C}}<$ , of which the negative pole is the more reactive. For example, in triphenylmethyl,  $\text{Ph}_3\text{CNa}$ , the anion is more reactive than the cation of  $\text{Ph}_3\text{CCl}$ . The fact that olefins may be classed as "anionoid" substances is supported by the experimental fact that they interact more readily with cationoid reagents, such as  $\text{Cl}$  or  $\text{NOCl}$ , than with anionoid reagents, such as sodium amide.

According to this concept carbonyl compounds are strongly cationoid, being ionized:  $>\text{C}=\text{O}< \rightleftharpoons >\overset{+}{\text{C}}-\overset{-}{\text{O}}<$ ; the negatively charged oxygen ion is relatively stable, whereas the  $\overset{+}{\text{C}}$  is very unstable and very reactive. Oxidizing and reducing agents are classified in a similar manner. Oxidizing agents are cationoid reagents acting as electron acceptors and reducing agents as anionoids by virtue of being electron donors. Halogens used as oxidizing agents act by absorbing two electrons:  $\text{Cl}_2 + 2e = 2\overset{-}{\text{Cl}}$ , and are accordingly cationoid reagents, while halogens active as halogenation agents yield one active cationoid ion and one inactive ion:  $\text{Cl}_2 \rightleftharpoons \overset{+}{\text{Cl}} + \overset{-}{\text{Cl}}$ .

The choice of the type of reagent, *i.e.*, the catalyst, will undoubtedly be influenced by the kind of reaction in which it is to participate, and will depend upon whether it is ionic or covalent. Ionic reactions are characteristic of solutions, especially those with solvents of high dielectric constant, such as water. They are influenced by the electrical polar environment of the molecule. The following will therefore be effective: (1) polar reagents such as sodium acetate, caustic potash or sulfuric acid; (2) polar catalysts such as acids or bases (in homogeneous catalysis); and (3) polar surfaces such as copper, alumina, etc. (in heterogeneous catalysis).

The non-ionic reactions are characteristic (1) of gases in which small dielectric constants interfere with the formation of ions, and (2) of processes in non-ionizing solvents of low dielectric constant, such as benzene or carbon tetrachloride. These reactions depend on the symmetrical rupture of a covalent bond, and the energy required for this is not derived from an electrostatic field, but from either radiation or intermolecular collisions, resulting in the origin of molecules with a high energy content.

In inorganic chemistry (chemistry of ions) chemical changes are rather instantaneous, whereas in organic chemistry (chemistry of bonds) rupture of bonds necessitates a lapse of time until molecules are brought into a state in which chemical changes may take place. In order to explain why chemical changes are not always instantaneous, Arrhenius<sup>1</sup> derived the equation  $K = Be^{-E/RT}$ , in which  $E$  is the energy of activation and  $B$  the reaction constant (which depends on the frequency of collision of the reacting molecules).

Moelwyn-Hughes,<sup>27</sup> bearing in mind the theory of activation of chemical changes, divides reactions into three groups: (1) reactions between ions: an ion pair or a covalent molecule is formed; the reaction is instantaneous

and  $E = 0$ ; (2) reactions between a covalent molecule and an ion: the reaction constant  $B$  is equal to the frequency of collisions  $Z$  between reacting components; and (3) reaction between two covalent molecules: the energy of activation  $E$  is very large, while the reaction constant  $B$  is much smaller than the frequency of collisions  $Z$ . It follows therefore that a definite amount of activation energy must be supplied before a covalent bond can be broken and that the activation energy  $E$  determines greatly the reaction velocity  $K$ . Reactions between two molecules in each of which covalent bonds must be activated are usually many hundred times slower than those between covalent bonds and ions, in which factor  $B$  is nearly equal to the frequency of collision of reactants and independent of their structures.

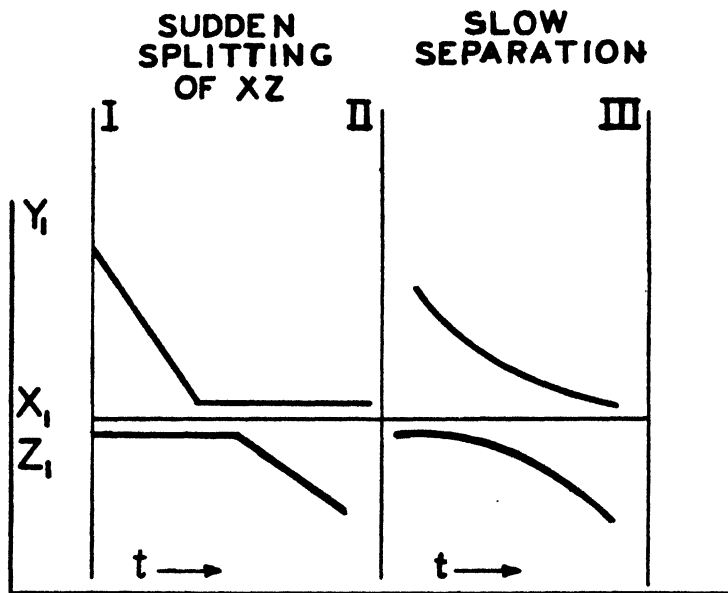


FIGURE 2.—Positions of Atoms during the Reaction.

It has been shown by Bradfield<sup>2</sup> that, for typically slow reactions, factor  $B$  is not altered by varying the nature of a polar substituent group in one of the interacting molecules, provided it is not in proximity to the point of reactivity. Williams and Hinshelwood<sup>43</sup> find evidence for the statement that the nature of the solvent used, as well as internal electronic displacement effected by substituents, may change considerably the activation energy  $E$ , but will have far less effect upon the factor  $B$  (reaction constant). Thus, general polarity will influence particularly the energy of activation of the chemical reaction. Obviously the controlling action of a catalyst must be viewed from the standpoint of its polar effect, also related to the activation energy in the Arrhenius equation:  $K = ae^{-q/RT}$  [Ber., 61, 1517 (1928)]. If the activation energy is essentially smaller than the splitting energy of a bond, the decomposition does not proceed through free atoms.

During collisions, a regrouping of electrons is effected under loosening of the bond as the result of the approach of another molecule. If the activation energy is smaller than the energy necessary for breaking the bond between  $X$  and  $Z$ , then the reaction  $Y + XZ \longrightarrow YX + Z$  does not proceed in the following two steps: (1)  $XZ \longrightarrow X + Z$ , (2)  $X + Z + Y \longrightarrow XY + Z$  and the bond between  $X$  and  $Z$  is set loose unless  $Y$  attacks  $XZ$ . Eyring and Polanyi<sup>6</sup> studied the problem concerning the manner in which loosening of bonds takes place, when  $Y$  flies toward  $XZ$ , in the direction of the line connecting the nuclei  $X$  and  $Z$ , and plotted the positions of single atoms as a function of time as presented in Figure 2.

London,<sup>25</sup> treating the problem theoretically, postulated that the total energy of the system  $XYZ$  depends only on the distance between single

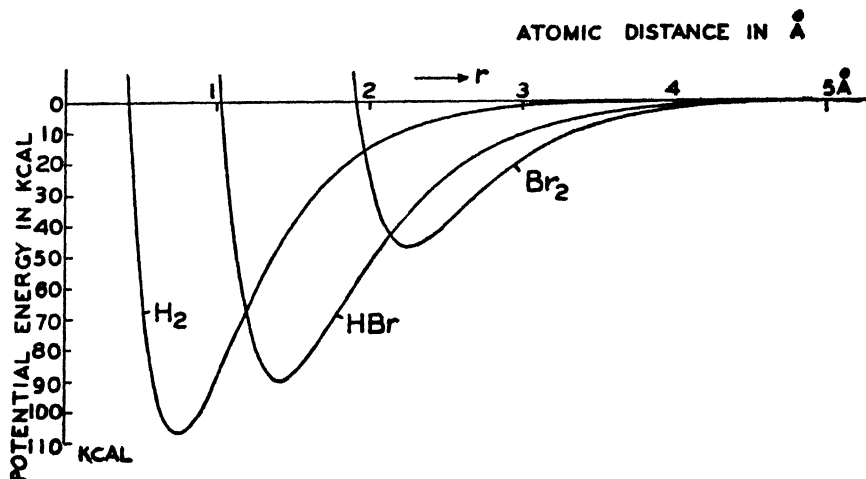


FIGURE 3.—Binding Energy (Potential Energy) as a Function of Nuclei Distance for  $H_2$ ,  $HBr$ , and  $Br_2$  Calculated according to Morse.<sup>28, 29</sup>

atoms, *e.g.*, the distance between  $Y$  and  $X$  and between  $Y$  and  $Z$ . Eyring and Polanyi calculated the binding energy for the reaction  $H + H_2$ ,  $H + HBr$ ,  $HBr + HBr$  and for the general case; to obtain the total energy of the system the binding energies  $XY$ ,  $YZ$  and  $XZ$  were considered as a function of distances between  $Y$  and  $X$  as well as  $X$  and  $Z$ . Plotting the atomic distances and the binding energy in the coordinate system, these investigators obtained energy in the form of level lines as shown in Figure 3.

It appears that the bond may be loosened and eventually ruptured by the presence of the reaction partner within the field of action, to reach which an energetic resistance must be overcome. Therefore it must be decided whether the reaction partner or the bonds are to be set loose, and whether the task is to be performed by substances from the outside or by definite molecular ingredients from the inside. It appears in all probability that  $Y$  would react essentially more easily if it were supported by loosening of the bond between  $X$  and  $Z$ .

A given bond does not require a definite amount of energy before it can react; rather, transition of energy is involved. If one of the bonds is in a

state of high vibrational energy while the other is in a state of low vibrational energy, the latter in all probability loses its energy, whereby the first gets enough energy to break, producing fragments having the same total energy content. Quantum mechanics provides numerical values both for all transition probabilities and for the control of the distribution of energy. Unless the reacting bond has concentrated within it almost all the energy necessary to induce a reaction it has, according to concepts of quantum mechanics, little chance of reacting.

Whether a given bond is primarily ionic or covalent, or between the two types, may be decided from ionization potentials and electron affinities. For example, the bond in NaCl is largely ionic because the ionization potential of Na is low and the electron affinity of chlorine is high. The bond in  $H_2$  is largely covalent, because the ionization potential is high and its electron affinity low. An intermediate case is represented by HCl, in which the bond partakes of both characteristics.

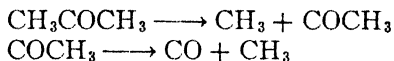
Pauling<sup>29b</sup> has shown that the distance between two atoms united by a valence bond is the sum of the corresponding atomic radii which depend on the nature of atoms themselves and the type of bond involved. If a molecule resonates among various structures, each atomic distance is about equal to the shortest calculated for any of the structures.

According to Pauling and co-workers,<sup>29b</sup> the energy of a molecule represented by a single structure is given fairly accurately by the sum of the energies of individual bonds contained in it. For molecules which cannot be represented by a single structure an extra resonance energy has to be evaluated from thermodynamic data.

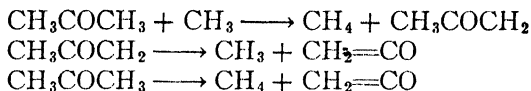
Rice<sup>29d</sup> regarded the decomposition of paraffins as a chain reaction initiated by free radicals formed by the primary scission of C—C bonds. Atomic hydrogen and radicals produced by the break-down of unstable fragments formed in the primary rupture of a C—C bond react with unchanged hydrocarbon molecules. The reactions of primary radicals with surrounding molecules constitute secondary reactions, which serve to initiate a cycle or chain of reactions, and do not determine directly the course of decomposition. On the other hand, the new radicals produced by their action with unchanged hydrocarbon molecules determine the composition of the reaction products. An attempt was made to evaluate the stability of bonds between individual atoms in hydrocarbons. It has been ascertained that in the case of methane the secondary and tertiary hydrogen atoms are bound more loosely than the primary. The strength of the primary C—H bond in  $CH_4$  is 93,000 cal., the strength of the secondary C—H bond in  $CH_4$  is 1,200 cal. less, and the strength of the tertiary C—H bond in  $CH_4$  is 4,000 cal. less than the primary. In the case of decomposition of pentane two processes are involved: (1) hydrogen atoms are separated from the molecules, and (2) C—C linkages are disrupted. The resulting radicals combine to form hydrocarbons with fairly long chains, among which hexane, nonane, and decane may be identified. The disruption of C=C and C—H linkages in the case of pentane may be effected by activated Hg atoms.

Kohanenko,<sup>14a</sup> studying the thermal decomposition of acetone at high

temperatures, postulated two mechanisms occurring simultaneously. The first is the chain mechanism. According to F. O. and K. K. Rice,<sup>29c</sup> the chain mechanism consists of a primary reaction:

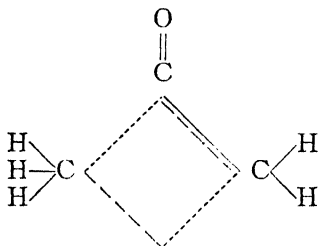


and a chain reaction:



The chain carrier is the free monovalent methyl radical,  $\text{CH}_3$ , and the rupture of the chain proceeds by recombination of methyl radicals.

The second mechanism postulated for the decomposition of acetone is that of the direct formation of methane and ketene as the result of an inner redistribution of valence bonds in the molecule. This mechanism, according to Patat and Sachsse,<sup>29b</sup> Patat<sup>29a</sup> and Sachsse<sup>32a</sup> is expressed by the following scheme:



in which the dotted lines denote the disrupted bonds, the broken lines represent the bonds formed and the solid lines denote the bonds remaining unchanged.

Kohanenko<sup>14a</sup> proposed a new method for detecting free radicals in the catalytic decomposition of acetone. The only direct method of detecting free radicals previously known was that of Paneth, which is based on the property of free aliphatic radicals reacting with metallic films with formation of highly volatile metal alkyls. A piece of metal (Pb, Zn, Sn, Sb) heated *in vacuo* forms metallic mirrors on the wall of the tube at a distance from the heated part of the tube where the decomposition is brought about. If the decomposition products containing free radicals are pumped out, the latter react with the metallic mirror; the metal alkyls formed are easily removed by pumping, and the mirror is seen to disappear gradually. This disappearance of the mirror is considered a direct proof of the presence of free radicals. But there are some disadvantages in this method, such as the difficulty in controlling the structure of the metallic mirror (some parts may be removed more easily than others), and the contamination of its surface by resinous substances originating in the course of the reaction. Also minute traces of oxygen may completely stop the removal of the mirrors as a result of oxidation. (Oxygen may induce the formation of resinous substances on the surface of the mirror.)

Kohanenko's method is based on the fact that recombination of

hydrogen atoms on the surface of an activated ZnS phosphorescent layer induces a bright luminescence.<sup>1a</sup> Kohanenko postulated that the recombination of free radicals would be followed by the same effects. Indeed the energy of recombination for the free radicals (the C—C bond strength) amounts to about 80 Cals., *i.e.*, of the same order as for hydrogen atoms (105 Cals.) and thus amply sufficient to excite a phosphorescent substance. Thus the presumed function of free radicals of inducing phosphorescence was used by Kohanenko to detect the chain carriers in the gas phase. The luminescence of the phosphorescent substance and the disappearance of the metal mirrors were recorded (bright enough and easily detected from 590–600° and upward at a distance up to 20 cm. from the furnace). Zinc sulfide preparations were activated with copper and two differently activated samples of calcium sulfide were used. Phosphorescent substances were found to be indicators of free radicals, being as sensitive as metallic mirrors. The luminescence of the phosphorescent substances observed in the decomposition of acetone was ascribed to the recombination of free hydrocarbon radicals. However, it is also recognized that luminescence may be due: (1) to heating of phosphorescent substances; (2) the action of ultraviolet light emitted as a result of some chemical process; and (3) a recombination of free hydrogen atoms.

Savard,<sup>3b</sup> discussing the role of the electron in chemical binding, assumes that binding energies may be expressed as  $D = 2n\gamma_m - \Sigma_{na}\gamma_a$ . In this equation  $2n = \Sigma_{na}$  denotes the number of electrons participating in the binding, and  $\gamma_m$  and  $\gamma_a$  are the corresponding ionization energies of the molecule and of the atoms. Thus the binding energy produced by an orbit with two electrons is equal to the sum of differences in the ionization potentials of the molecule and each of its atoms, whereby for each of these differences a total number,  $na$ , is a standing factor. The number for C = 4, for O = 2, for Cl = 5, for S = 4. Thus the binding energy of Cl<sub>2</sub> is  $2 \times 5$  of the difference  $\gamma_{Cl_2} - \gamma_{Cl}$ ; the same number 5 is obtained, for instance, for HCl from spectroscopic data.

For a molecule consisting of many radicals the binding energy is expressed as follows:  $D = \Sigma_{2n}\gamma_m - \Sigma_{na}\gamma_a$  with  $\Sigma_{2n} = \Sigma_{na}$ . To the radical is ascribed the same ionization potential as that of the free atoms, for example, CH<sub>3</sub> has the ionization potential of C. The total binding energy of ethane is then: (1) the ionization potential of twice 6 electrons of the CH<sub>3</sub> binding; (2) the ionization potential 12.8 of 2 electrons of the CH<sub>3</sub>—CH<sub>3</sub> bond. From this is subtracted the ionization potential 11.26 V of 8 electrons of 2 C atoms and that of 6 electrons of the 6 atoms—13.54 V. Thus  $D = 12 \times 14.4 \text{ V} + 2 \times 12.8 - (8 \times 11.26 + 6 \times 13.54) = 27.08 \text{ V}$ , where  $\gamma_{CH_4} = 14.4 \text{ V}$ .

Rossini<sup>31</sup> determines energies of atomic bonds in methanol and ethanol from measured combustion heats for changes in the heat content  $W$  in the formation of gaseous CH<sub>3</sub>OH from CH<sub>4</sub> (gas) + 1/2O<sub>2</sub> (gas) at 298° absolute.  $AW_{298^\circ} = -30.24 \pm 0.09 \text{ k.cal./mol.}$ , and for the corresponding formation of gaseous C<sub>2</sub>H<sub>5</sub>OH from C<sub>2</sub>H<sub>6</sub> + 1/2O<sub>2</sub>,  $AW_{298^\circ} = -36.09 \pm 0.15 \text{ k.cal./mol.}$  These results indicate that to disrupt a C—H bond and to introduce an oxygen atom into the molecule, CH<sub>3</sub>R (formation of CH<sub>3</sub>OH), an energy

is required which depends entirely on whether  $R=H$  or  $R=CH_3$  is dealt with. Thus, contrary to the usual assumptions, atomic binding energies are not additive in these compounds and their homologs. Even in the case of paraffins the binding energy is greatly influenced by the nature of the substituent radical.

In another paper Rossini<sup>32</sup> states that if Pauling's postulate of constancy of atomic binding energies should be fulfilled for normal paraffins of the type formula,  $C_nH_{2n+2}$ , then the following relationship should exist for the splitting ability of gaseous molecules in  $nH$  atoms and activated  $C$  atoms:  $D_0 + nE_C = (2n + 2)a + (n - 1)b$ , where  $E_C$  is the agitating energy of  $C$  atoms;  $a$ , the energy of the  $C-H$  bond;  $b$ , the energy of the  $C-C$  bond and  $D_0$  the splitting ability expressed exclusively in  $n$  atoms (at  $0^\circ$ ). On the basis of combustion heat measurements of the first 5 paraffins the values received for the left side and the right side of the equation are:

$CH_4$	=	$4.81 \pm 0.08$
$C_2H_6$	=	$0.80 \pm 0.07$
$C_3H_8$	=	$0.27 \pm 0.06$
$C_4H_{10}$	=	$0.12 \pm 0.07$
$C_5H_{12}$	=	$0.03 \pm 0.08$
$C_nH_{2n+2} (n > 6)$	=	$0.00 \pm 0.11$ k.cal./C atom

Thus the splitting work of the gaseous paraffins is a linear function of  $n$ —only above  $n = 6$ ; deviations lie in the direction of a greater stability of the molecule and reach their highest value for  $CH_4$ . If all the binding energies of  $C-H$  and  $C-C$  bonds in a given molecule were equivalent to one another, then it must be concluded that for  $n < 6$  the strength of one or the other bond or both bonds increases with decreasing  $n$ . It is Rossini's belief that various kinds of  $C-H$  as well as  $C-C$  bonds should be differentiated in the  $n$ -paraffins, for instance, three kinds for each bond,  $a_0, a_1, a_2$  as well as  $b_0, b_1, b_2$ , and the bonds at the ends of the molecule should be energetically different from those in the middle of the molecule. This should be considered in formulating a general relationship for the total binding energy.

Zahn,<sup>44</sup> considering Rossini's work in which he ascertained a deviation from the additivity of chemical energies by building up complex molecules in the case of paraffins and alcohols, gave an empirical point of view with regard to the significance of binding energy. If the formation energy is to be built up from binding energies and the reciprocal action between the bonds, then both parts of energy are still unknown with regard to the thermochemical data. Zahn postulates that for the reciprocal action between bonds an apparent additivity of building energies is obtained, from which apparent binding energies may be defined. In case the additivity law does not hold true, the formation energy may be expressed through the apparent binding energy and an additional member. A general discussion of atomic and binding energies led Zahn to the assumption that the energy corresponding to movement (heat content + zero point energy of vibrations) composes one-tenth of the total formation energy. Zahn proposes also to study the regularities of the formation energy due to structure and thus introduces the concept of "electronic energy."



Magnetism and chemical binding in intermetallic phases are linked by Vogt<sup>42</sup> to binding caused by electrons which have the same kind of binding relation toward many atoms. These binding electrons as well as the conductivity electrons belong to the totality of atoms in the metal and not to a definite pair of neighboring atoms, as in the case of homo-polar valence binding. Thus the concept of chemical binding may be estimated through the number of valence electrons per atom. It has been recognized that while a number of reactions are brought about by ionic reagents (catalysts) and may be attributed therefore to the ionization of covalent bonds, there is another group of reagents with an odd number of valence electrons. The quantized "spin energy" of the odd electron gives to the atom a definite magnetic moment which has been measured by the method of Gerlach and Stern<sup>10</sup> and determined for the hydrogen atom, nitric oxide and nitrogen.<sup>14</sup> Lewis<sup>24</sup> has stated that all compounds whose molecules contain an odd number of electrons should be paramagnetic. On the other hand, atoms or molecules containing an even number of electrons are usually found to have no magnetic moment, their electrons being associated in groups containing equal numbers of electrons with spins of opposite signs.

The quantum state to which electrons in free atoms belong is of significance, since it has been found that the quantum and ionization states are not the same for all phases, nor for all structures in which a metal participates in the reaction. For example, Pd as a neutral atom is diamagnetic and as an ion, paramagnetic; the pure metal splitting off conductivity electrons is paramagnetic. Palladium dissolves diamagnetically in copper, silver and gold and is not ionized in such solutions. The diamagnetism of Pd—H alloy indicates the presence of a complex  $\text{PdH}^+$ . Other transition metals alloyed with copper, silver and gold show analogous behavior. Usually in ferromagnetic alloys the magnetic property is characteristic of the ionization stage of added metals in mixed crystal formation. Palladium dissolves in nickel as a  $\text{Pd}^+$  ion and not as a neutral atom. Thus magnetic studies may be a means of classifying the structure of metallic systems used as catalysts.

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## PART II

### Catalytic Oxidation

Since almost every oxidation may be viewed to a certain extent as a splitting off of hydrogen from the substrate, oxidation and dehydrogenation in catalytic processes have been discussed together. It has often been emphasized that preliminary dehydrogenation plays an important part in oxidation processes.

Various hypotheses have been suggested for the interpretation of the mechanism active in catalytic oxidations. The investigations of Schonbein<sup>37, 38, 39, 40, 41, 42</sup> and of Traube<sup>44</sup> led to the conclusion that, in oxidation processes involving air or other substances containing oxygen, an intermediate substance is formed, which has a stronger oxidizing ability with respect to the substance to be oxidized. A phenomenon termed "activation of oxygen" has been postulated as one preceding catalytic oxidation. If the helping substance, after giving off a part of the "activated" oxygen, remains in an oxidized state unable further to adsorb oxygen, an induction reaction is involved, since comparable amounts of both helping and reacting substances are constantly subject to oxidation. If the helping substance gives off all the adsorbed oxygen to the reactant and is regenerated to its original form, after which it is capable of re-adsorbing oxygen, a catalytic process is involved in which small amounts of the helping substance convert large quantities of the reacting substance. Van't Hoff considered the probability of an electro-polar splitting of oxygen molecules in oxidation processes, and assumed that electro-polar properties are characteristic of the active form of oxygen. Bach<sup>1, 2, 3</sup> and Engler<sup>13, 14, 15</sup> stated that in the course of the reaction more active and faster-acting oxidation agents are formed from molecular oxygen and the components of the reaction system, and that these are primary peroxides. Engler and his co-workers isolated primary peroxides and showed quantitatively that in

the oxidation of triethyl phosphine the adsorption of oxygen corresponds to the formation of a peroxide  $(C_2H_5)_3PO_2$ .<sup>12</sup> In the oxidation of dimethyl fulvene  $(C_8H_{10})$  Engler ascertained the intermediary peroxide formed  $(C_8H_{10}O_4)$ . Furthermore, Bacyer and associates<sup>6, 7, 8, 9</sup> have proved that organic peroxides are formed in the oxidation of turpentine oil.

Investigating the auto-oxidation of linoleic acid and its esters present in linseed oil, Goldschmidt and Freudenberg<sup>16</sup> found that the total oxygen taken up by the unsaturated acid and its esters in the presence of Co catalyst is added as a peroxide on the double bond. In this case the peroxide formed is very stable. If linseed oil contains various components in addition to the linoleic acid esters, a part of the peroxide formed is used for the oxidation of the accompanying substances. However, Slansky,<sup>43</sup> studying the oxidation catalysis of linseed oil, stated that the theory of intermediate reactions between the catalyst and the reacting substances in this case is doubtful, because there is no primary adherence of oxygen to the catalysts. Working with a series of catalysts soluble and insoluble in linseed oil, he observed that base-forming metals and their salts always accelerate the oxidation of this oil. The stronger action of catalysts of a pronounced basic character has been explained by the assumption that the

completely saturated acid groups,  $C \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$ , of the glycerides should be in-

fluenced by the basic affinity forces of the catalysts. The basic catalyst does not increase the reaction ability of oxygen, although it accumulates oxygen primarily, but it increases the reaction ability of the double bond

in the glyceride molecule by action upon the acid group,  $C \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$  Portrayed

in space, the glyceride molecule has two poles, namely, a glycerin pole with

three acid groups,  $C \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$ , and one  $CH_3$  pole, in the close vicinity of which

are placed the active double bonds. In accordance with the Harkins and Langmuir orientation theory, it is postulated that the less active groups are directed toward the vapor phase; therefore the less active (glycerin) pole of the glyceride molecules present at the surface of the linseed oil is directed toward the air, and the  $CH_3$  pole with the more active double bonds is turned toward the inside of the liquid. It is furthermore deduced that the oxidation of linseed oil proceeds relatively slowly when the double bonds are withdrawn from the direct attack of the oscillating oxygen molecules. In the case of basic catalysts present in colloidal form, or coarsely distributed, the glyceride molecules are adsorbed by the particles of the catalyst and directed toward them, and the glycerin poles containing the

$C \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$  groups are directed toward the catalyst, while the  $CH_3$  poles are turned toward the air.

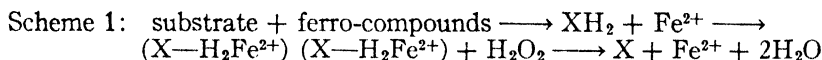
In such manner the double bonds are closer to the sphere of attack by

the vibrating oxygen molecules and the oxidation process of the oil is therefore accelerated. Should the substances added to linseed oil as catalyst be directed in the opposite way so that the double bonds are less exposed to the attack of the oxygen molecules, the oxidation of the linseed oil may be even slowed down. On the other hand, Slansky considers also the oxophilic nature of metallic salts as a factor determining their catalytic action. Oxophilic substances opposing carbophilic substances containing preferentially carbon<sup>17</sup> are those containing oxygen and adsorbed by adsorbents rich in oxygen. If into the linseed oil is introduced a boundary rich in carbon, then the carbon-rich  $\text{CH}_3$  poles would direct themselves toward it and the oxidation would be retarded. As a matter of fact, lamp-black, graphite, asphalt, and many organic dyes slow down the oxidation (drying) process of linseed oil. Since the glycerin pole not only possesses the acid character but is also oxophilic because of the six oxygen atoms accumulated, both basic and oxophilic forces act upon it; and a layer of linseed oil with starch dries only slightly more slowly than that with  $\text{BaSO}_4$  as catalyst. Thus, through accumulation of oxygen the glycerides become oxophilic, form a colloidal solution in the linseed oil, and act as such upon the glycerin pole of the glyceride molecule.

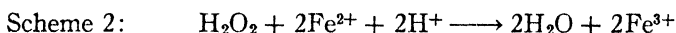
The catalytic action of metal catalysts considered as inductors has been interpreted as based on intermediary addition of oxygen as well as primary oxide or peroxide formation. Job<sup>19, 20</sup> found the formation of a peroxide,  $\text{CeO}_3$ , in the oxidation of cerium salts. In the oxidative transition of aromatic hydroquinone into anthrahydroquinone, or of hydrazo- bodies into quinones or azo- bodies, Manchot<sup>25, 26, 27</sup> assumed as the first reaction step the addition of the labile H atom of the reacting substance to an unsplit oxygen molecule, with formation of hydrogen peroxide as expressed by the scheme:  $\text{AH}_2 + \text{O}_2 \longrightarrow \text{A} + \text{H}_2\text{O}_2$ . By using as an acceptor  $\text{Ba}(\text{OH})_2$ , Manchot actually proved the presence of the peroxide through the formation of the difficultly soluble  $\text{BaO}_2$ . Manchot likewise considered as a characteristic step in the primary oxidation of metal compounds the formation of excessively oxidized molecules, exceeding the normal valence step, as in the oxidation of  $\text{Ti}(\text{OH})_3$  by  $\text{O}_2$  in an alkaline solution as compared with a normal oxide,  $\text{Ti}(\text{OH})_4$ . Other reactions with excessively oxidized iron compounds were claimed by Manchot and Herzog<sup>29</sup> and Manchot and Glaser<sup>28</sup> (the primary iron oxides considered were  $\text{FeO}_2$  as well as  $\text{Fe}_2\text{O}_3$ ). For the reaction of  $\text{Fe}''$  salt and  $\text{H}_2\text{O}_2$  in a neutral solution in the presence of KI as acceptor, Manchot and Lehmann<sup>30</sup> found for each disappearing  $\text{Fe}''$  ion [converted into  $\text{Fe}(\text{OH})_3$ ] about 3 equivalent  $\text{O}_2$  present for the oxidation of the iodine ion. The fact that the back formation of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  contrary to systems  $\text{Fe}^{2+} + \text{H}_2\text{O}_2$  and  $\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{HI}$  does not take place has been considered as proof of the formation of  $\text{Fe}_2\text{O}_3$  as an intermediate oxide. Manchot derived from his investigations the conclusion that the helping substance is led back into the initial form (in the case of iron compounds to the ferro form) and that this is steadily active in "transference" of oxygen because the activity of the "transferer" is being renewed. According to Manchot and Pflaum,<sup>31</sup> the primary oxides of metals may serve as acceptors not only in oxidations with elemental

oxygen as well as in auto-oxidations, but also in the case of such oxidants as chromic, permanganic and hypochloric acids as well as hydrogen peroxide.

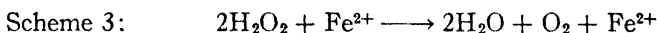
The hydrogen peroxide oxidation over iron catalyst has been interpreted by Wieland as consisting in the action of ferro- compounds in such a manner that readily dissociating complexes are formed with the reacting molecules (substrate), and the hydrogen atoms set free thereby hydrogenate  $\text{H}_2\text{O}_2$  to water according to scheme 1:



The reaction stops due to side reactions, and the active form of the  $\text{Fe}^{2+}$  catalyst is converted in the catalytically non-active ferri-form according to scheme 2:

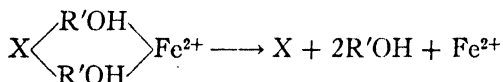
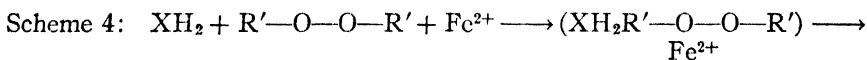


Similarly,  $\text{H}_2\text{O}_2$  before being rendered active as an acceptor for  $\text{H}_2$  of the substrate according to scheme 1 may decompose catalytically over  $\text{Fe}^{2+}$  according to scheme 3:



Thus, according to Wieland, the extent to which the substrate is catalytically oxidized depends upon the relative velocities of concurrent reactions 1, 2 and 3. In systems in which ferri- compounds are converted into the ferro- form through the reducing action of the reacting molecules (substrate) in spite of the presence of  $\text{H}_2\text{O}_2$ , reaction (2) is not injurious for the final effect and catalysis takes place (oxidation of hypophosphite with  $\text{H}_2\text{O}_2$ ). In case the regeneration of  $\text{Fe}^{2+}$  is impossible, the oxidation process is of the type of an induced reaction (oxidation of formic acid).

Wieland and Bossert<sup>50</sup> gave the scheme for the oxidation of phenols and hydrazobenzenes by means of diethyl peroxide instead of  $\text{H}_2\text{O}_2$  over iron catalyst. The activating action of  $\text{Fe}^{2+}$ , being similar in both cases, consists in the activation of the peroxidic bond  $-\text{O}-\text{O}-$ , as well as in loosening the bond of H atoms able to split off in the substrate according to scheme 4:



It is assumed that for definite types of catalyzed as well as induced oxidation reactions, the activation of the oxidation agent is just as essential as the activation carried out by the catalyst with respect to the substrate.

Discussing the course of the reaction in the oxidation of orthophosphorous acid to phosphoric acid by hydrogen peroxide, which is similar to Fenton's reaction of the oxidation of tartaric acid over ferro- salts as catalysts, Nerz and Wagner<sup>34</sup> assume that the oxygen is transferred from hydrogen peroxide to orthophosphorous acid, and that the ferro- ion is trans-

ferred in an optional repeated reaction chain over suitable intermediate steps of iron whereby the ferro- ion is regenerated. The splitting of the chain is caused by the conversion of a ferro- ion or one of its intermediate products into a ferri- ion, which does not have the ability to transfer oxygen. The reaction course may be followed by determining the conversion ratio of hydrogen peroxide to the ferro- salt by changing the concentration of single components in the reaction. In the absence of air, it has been observed that the converted amount of hydrogen peroxide increases proportionally to the added amount of the ferro- salt and approaching then a certain limit. Hydrogen peroxide appears to play an advantageous part in the splitting of the chain. Rapid introduction of a ferro- salt solution causes an increase in the concentration of the chain carriers and effects their mutual destruction. On the other hand, it has been ascertained that air or oxygen when present function chiefly by discontinuing the reaction chain.

In a certain opposition to Engler's and Bach's and also to Manchot's theory of the intermediate peroxidic products, stands Wieland's<sup>10, 23, 24, 49</sup> dehydrogenation theory for the explanation of oxidation processes in catalysis. Wieland considers significant in oxidation catalysis not the increase in the action of the oxidizing agent or the formation of an active oxygen brought about by the catalyst, but rather the increase in the reduction ability of the substances to be oxidized. The function of the catalyst in taking up oxygen either directly or from the oxidation agent and in transferring it to the substrate is conceived as a loosening and removal of hydrogen from the substrate (the substance to be oxidized), so that the latter may at once readily undergo oxidation through the molecular oxygen or the oxygen contained in the oxidizing agent.

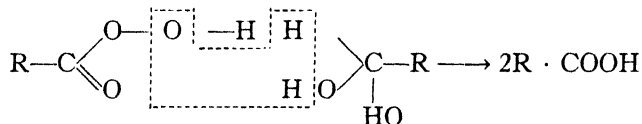
Wieland's viewpoint is illustrated in examples of catalytic oxidation of organic substances such as formic acid, the molecules of which contain hydrogen which can be split off with relative ease. The typical dehydrogenating contacts, such as Pt and Pd, have to perform a double task, *i.e.*, (1) to split off the hydrogen from the substrate molecule, and (2) to bind the hydrogen set free by the oxygen present. Wieland<sup>47, 48</sup> considers as hydrogen acceptors not the typical oxygen-containing oxidizing agents, but substances especially adapted for taking up hydrogen, such as quinone, quinone derivatives, and methylene blue. Other hydrogen acceptors are hydroquinone, hydrazobenzene, dihydronaphthalene, and dihydroanthracene in the presence of palladium black, which may be oxidized to their dehydro- compounds in the absence of air. It has been stated that organic compounds containing hydroxyl or amino groups, such as carbohydrates, oxy-acids, phenols and amino acids or aniline, may be converted into oxidation products with dehydrogenation catalysts such as Pd or Pt black in the absence of oxygen and in the presence of quinone or methylene blue. In the case of compounds not containing hydrogen atoms which are easily split off, Wieland assumes the dehydrogenation of their hydrogenation forms. Thus, for example, the conversion of aldehydes into acids should occur during dehydrogenation of the aldehyde-hydrates. Oxidation of aldehydes to acids may be carried out, however, without oxygen in the

presence of benzoquinone or methylene blue as acceptors of hydrogen. Thus oxidation of CO to formic acid should take place through CO hydrate. Oxidation of SO<sub>2</sub> should occur through sulfurous acid.

Metal contacts which are good catalysts for hydrogenation or addition of hydrogen were believed to be good examples of the dehydrogenation theory in the case of heterogeneous oxidation reactions. From thermodynamic principles it follows that substances accelerating hydrogenation should catalyze dehydrogenation also. Later works by Wieland<sup>51, 52</sup> seem to indicate that both reasonings, namely, that of the activation of the oxidizing agent as well as that of labilizing the hydrogen in the substrate, may be correct in the interpretation of the function of catalysts in oxidation reactions. The mechanism of metal action in the auto-oxidation of aldehydes has been modified by Wieland to the extent that he assumes the Fe<sup>2+</sup> ions form labile complexes with the molecules of the substrate; they add themselves to the C=O bond and activate it. In the case of hydrogenated

forms, they are supposed to go to the  $\text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{OH} \\ \diagdown \\ \text{OH} \end{array}$  group and labilize two of its

hydrogen atoms. The activated, non-hydrogenated heavy metal-aldehyde complexes are able to react rapidly with oxygen molecules, forming per-acids according to the following scheme:

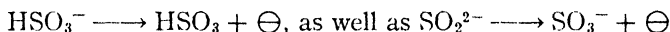


From one molecule of the aldehyde hydrate, two molecules of normal acid are obtained.

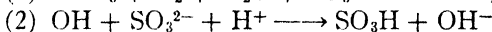
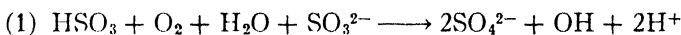
The probability of a simultaneous intermediate formation of peroxides in the form of per-acids and dehydrogenation of the reacting molecules has been recognized. Wieland himself has proved, contrary to his initial assumption of a pure dehydrogenation of the aldehyde hydrate, that in an aqueous solution phenylglyoxal, occurring only in the form of its hydrate, undergoes no auto-oxidation over iron compounds as catalysts, but passing it through benzo per-acid converts it readily into the acid.

Some catalytic oxidation reactions, similar to exothermal conversions in gaseous systems, proceed in the form of a chain, while others are rather of the type of induced reactions. In the latter processes the substance acting as inductor does not remain unchanged, like a true catalyst, but participates chemically following definite stoichiometric relationship. The function of a catalyst in oxidation processes occurring in liquid media possessing a chain-like reaction course is understood to be the release of relatively long chains, which may cause considerable conversions. Thus oxidation reactions in catalysis have been interpreted by Backström<sup>6</sup> through the assumption of reaction chains in which reactive intermediate products of a radical type are detected. He considered the auto-oxidation of the aldehyde up to the per-acid step, or the auto-oxidation of a sulfite solution, as examples of chain reactions.

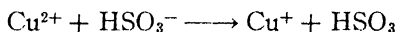
According to Backström<sup>4</sup> there are three agents: (1) metal sulfide ions; (2) adsorbed ultraviolet radiation, and (3) oxidation agents which influence the sulfite solution by helping to decrease the reaction resistance of salts of sulfurous acid with respect to the dissolved elemental oxygen. Through the attack of these agents an especially reactive radical originates from the sulfite molecule, which functions either by causing an impulse or in the sense of propagating the oxidation chain. All three agents are thought to perform their action by effecting a separation of electrons from the anions of the sulfite, following the scheme:



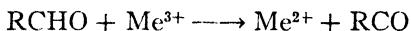
Among heavy metal ions chiefly  $\text{Cu}^{2+}$  is considered as a suitable catalyst in oxidizing the sulfite, and the radical formed by the splitting off of an electron is monothionic acid ( $\text{HSO}_3$ ). According to Haber this radical, in the presence of dissolved oxygen, brings about a chain reaction of the following type:



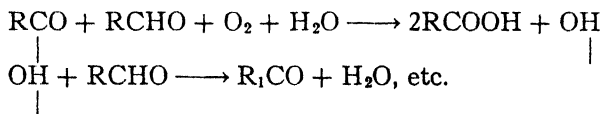
$\text{OH}$  and  $\text{SO}_3\text{H}$  radicals are representative examples of active chain members. When a sulfite solution free from oxygen is subjected to an ultraviolet radiation in a partial anodic oxidation, monothionic acid is formed, and this effects a considerably faster conversion of the remaining amounts of sulfite with elemental oxygen. The action of metal ions is similar. First the  $\text{SO}_3\text{H}$  radical is formed and then the  $\text{Cu}^{2+}$  ions produce an impulse for the chain formation as shown in the equation:



(with reduction of the cupric ion to the cuprous ion). For the oxidation of aldehydes to acids Haber and Willstätter<sup>18</sup> assume the same kind of chain mechanism, except that in this case the dehydrogenation takes place according to the scheme:



and is the step introducing single chains. Thereafter the following reactions take place:



They believe a peroxide in the form of a radical  $\text{R} \cdot \text{CO}$  is formed in the intermediate stage of the reaction.



Marek and Hahn<sup>32</sup> assume that oxidation of alcohols to aldehydes is promoted by catalysts in either one of two ways: (1) metal oxides catalyze a straight oxidation wherein a large excess of oxygen is involved, and (2) metals of the hydrogenating type carry out the oxidation in two steps

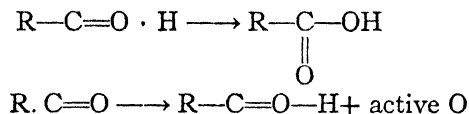


or produce a "coupled" reaction, and the amount of oxygen required therein is less than the calculated theoretical value, although the same end point is attained in the oxidation process. The first stage in the reaction is considered to be the endothermic decomposition of alcohol into the aldehyde; in the second stage hydrogen reacts with oxygen forming water in an exothermic reaction, so that the energy for the first stage is supplied by the second stage. Nickel catalyzes both stages of the reaction.

It appears that catalytic oxidation reactions are concerned not only with taking up oxygen:  $\text{CH}_3\text{CHO} \longrightarrow \text{CH}_3\text{COOH}$ , but with dehydrogenation as well:  $\text{CH}_3\text{CH}_2\text{OH} \longrightarrow \text{CH}_3\text{CHO}$ . Accordingly it is stated that variation in the course of the reaction may be introduced not only through a stepwise oxygen attack of single groups in the molecule to be oxidized but through a possible change in the sequence, in which various single groups of the compound to be oxidized are subjected to a partial or complete oxidation or dehydrogenation. Variations in the transitions of an oxidation process may be due also to other factors such as temperature, concentration, pressure conditions and not least to whether the oxygen used is in an elemental or chemically bound state. The kind and amount of the catalyst, as well as other factors, are to be considered. Catalysts function in oxidation processes not only by increasing the speed at a certain temperature, but also by reducing the effective temperature at which the process may take place. As in other types of catalytic reactions both the active catalyst and the selected physical conditions regulate not only the velocity and direction of the oxidation, but the extent of the oxidation as well, yielding stable and uniform reaction products.

Prévost,<sup>35</sup> considering organic bonds the strongest bonds of all and coördinative bonds of complex compounds still quite strong, points out that bonds of molecular association, such as those characteristic of electrovalences, are very weak (the more so, the smaller the charge of ions) and that therefore, in the case of inorganic compounds containing oxygen, the bivalence of oxygen should not be maintained in all cases. Thus, for example, considering the active oxygen atoms originating on decomposition of peroxides, Prévost assumes the existence of a monovalent oxygen. The splitting of peroxides  $\text{R}-\text{O}$  takes place in such a manner that R is converted into a neutral molecule, while O becomes an active oxygen atom with an incomplete octet of electrons. The oxidizing ability of the peroxide molecule  $\text{R}-\text{O}$  is stated to depend on the ease of splitting. Therefore the oxidizing ability of oxides of metalloids having a monovalent oxygen is considered to decrease from right to left and from top to bottom in the periodic system of elements. Furthermore the oxidizing ability is the smaller the more oxygen atoms are bound to the metalloid. Prévost also shows exceptions to his rule, namely, that hypochlorites decompose directly into chlorides and chlorates without first changing into chlorites. As this indicates that hypochlorites are weaker oxidizing agents than chlorites, it is contradictory to the above generalization. Actually hypochlorites and hypochlorous acid do not possess in their ordinary form,

ClONa and ClOH, the monovalent oxygen as the higher oxidation step. If the molecule possesses reducing properties, the originating oxides are not peroxides. Prévost expressed the oxidation of aldehydes as follows:



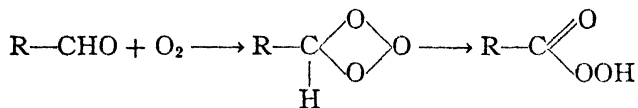
Prévost states also that an oxidizing molecule which has no monovalent oxygen may oxidize only if previously tautomerized. Thus, according to his conceptions, the stable form of  $\text{H}_2\text{O}_2$ , expressed as  $\text{H}-\text{O}-\text{O}-\text{H}$  must

tautomerize to  $\text{O}-\text{O} \begin{array}{l} \text{H} \\ \diagup \\ \diagdown \\ \text{H} \end{array}$  in order to act as an oxidizing agent.

Considering Brewers' observation that ions are formed in the oxidation of alcohol by air, Coçosinskhi<sup>11</sup> postulated the possibility of the existence of an electrostatic charge on the catalyst and supported this assumption by experimental evidence. A mixture of alcohol and air was heated to 50° and passed over an electrically heated copper tube (20–400°) in which a platinum spiral serving as catalyst was placed axially and connected with an electrometer. As a result of the reaction a charge of –1.3 to 13.0 volts was measured on the catalyst. The electrostatic phenomenon has been interpreted by assuming that through a greater mobility of positive ions an agglomeration of negative ions takes place on the surface of the catalyst, and that during the reaction an adsorption compound originates which influences the electrostatic equilibrium in the sense of favoring ionization. In agreement with this, Coçosinskhi showed the existence of negative hydrogen ions in the gas stream.

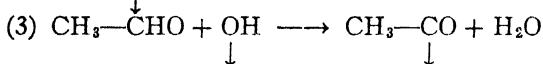
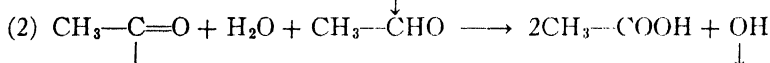
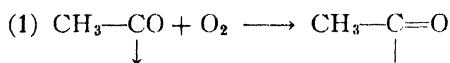
The course of the oxidation reaction has been described as follows. First of all on the contact surface activated oxygen atoms are present which react in pairs with one alcohol molecule and form a complex containing two hydroxyl groups on the surface. Then as a result of their decomposition a negative  $\text{H}_2\text{O}$  ion originates. Whether other ions are parts of the alcohol molecules has not been established.

Rieche,<sup>36</sup> discussing oxidation of various organic compounds with atmospheric oxygen, concluded that the addition of oxygen to the double bond is improbable and that O<sub>2</sub> is rather shifted between C and H. Oxidation of aldehydes with atmospheric oxygen over Fe, Co, or Mn salts, according to Engler and Weiszberg<sup>13</sup> has been explained by the addition of O<sub>2</sub> to the C=O bond of the aldehyde with formation of an intermediate product, a per-acid:

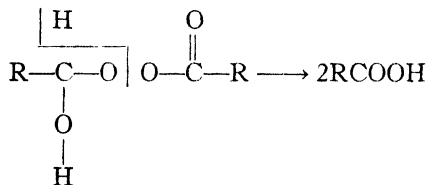


Rieche believes that, since the addition of  $O_2$  to the  $C=O$  bond is not probable because aldehyde hydrate also forms a per-acid with  $O_2$ , his con-

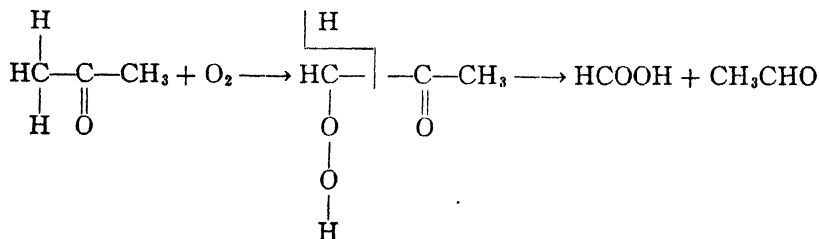
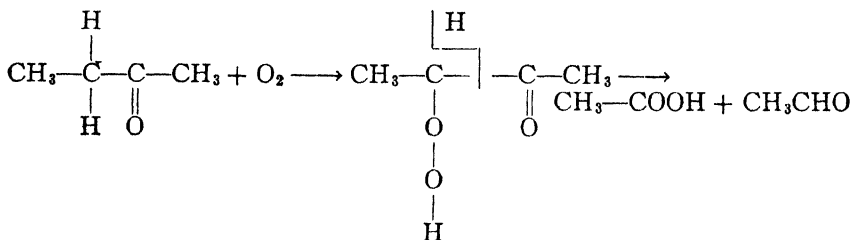
ception that the hypothetical radicals  $R-\overset{\text{O}}{\underset{\text{<}}{\text{C}}}$  and H are added to  $O_2$  is justified. The same follows from the standpoint of the radical chain theory outlined by Frank, Haber and Willstätter when applied to aldehyde oxidation:



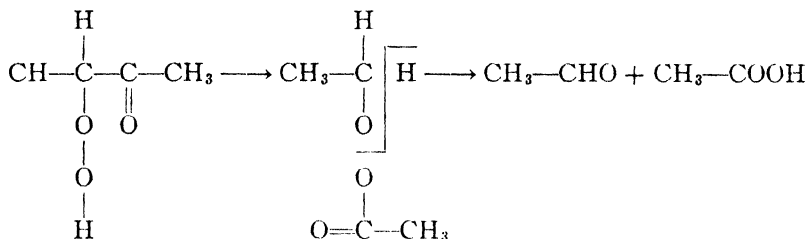
Per-acid gives with the aldehyde a decomposable peroxide as an intermediate product, which suffers an intermolecular disproportioning as shown in the equation:



Rieche applied his viewpoint of intermediate shifting of  $O_2$  between R and H also to the oxidation of ketones, expressing it as follows:



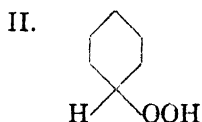
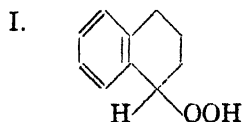
Hydroperoxy-ketones are assumed to be the intermediate products, these undergoing a disproportioning into acid and aldehyde under the influence of metal salts. The aldehyde is then oxidized further through atmospheric oxygen to the acid. However, it is likewise possible that hydroperoxy-ketones are converted into per-acid esters due to a place change of the acyl group and a hydrogen atom, which is then disproportioned to acid and aldehyde as shown in the scheme:



With respect to the oxidation of olefins, two types of reaction were differentiated: (a) the C=C bond reacts with the addition of O<sub>2</sub> and formation of polymer peroxides, and (b) organic substances are added to the oxygen molecule by splitting of a R—R or R—H bond following these schemes:

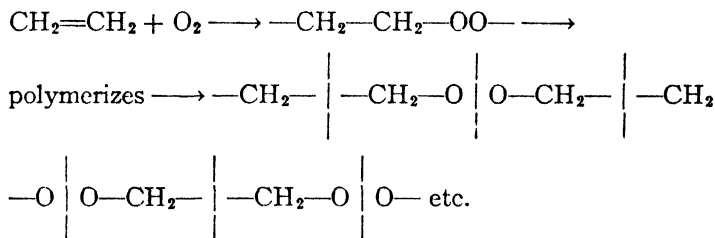
- (1)  $\text{R}-\text{R} + \text{O}_2 \longrightarrow \text{R}-\text{OO}-\text{R}$
- (2)  $\text{R}-\text{H} + \text{O}_2 \longrightarrow \text{R}-\text{OO}-\text{H}$
- (3)  $2\text{R}-\text{H} + 2\text{O}_2 \longrightarrow \text{R}-\text{OO}-\text{R} + \text{H}_2\text{O}_2$

The formation of R—OO—R may be presumed only for O<sub>2</sub> reacting under conditions under which formation of the radical R is possible, for example, at room temperature only in the case of dissociating ethanes. However, at high temperatures radical dissociation and addition in the above sense is a problem in the case of almost all organic substances. Rieche points out that the intermediate shifting of O<sub>2</sub> between C—H under moderate conditions may be considered for all substances in which an activation of the C—H bond takes place by reason of the molecular structure. Rieche emphasizes that in most cases the action of O<sub>2</sub> differs greatly from that of O<sub>3</sub>, and that O<sub>2</sub> in many cases does not attack organic substances at the double bond, but quite often shifts between a double bond or the C—H bond in the neighborhood of the oxygen. The double bond may also take up O<sub>2</sub> while it activates the C—H bond. The alkyl groups are usually difficultly oxidized; the neighborhood of an aromatic group, for example, toluene, or of an oxygen atom (alcohols, ether) may be of assistance in the reaction. (The presence of the ethylene group has a similar influence.) Tetralin and cyclohexene oxidize, as is known, to the peroxides (I) and (II).

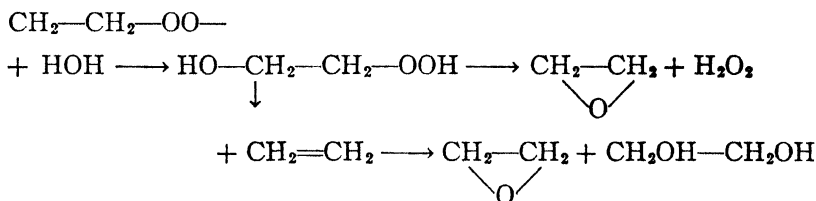


The oxidation products of simple unsaturated hydrocarbons very often possess the same characteristics as those of hydroperoxides.

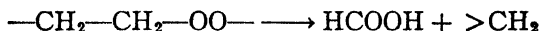
Rieche<sup>46</sup> attempted to interpret the process of ethylene oxidation in which, as stated by Lenher,<sup>22</sup> ethylene oxide, glycol glyoxal, formaldehyde, formic acid, water, carbon monoxide, carbon dioxide, hydrogen and dioxymethyl peroxide, but no acetaldehyde are formed. The course of the reaction proposed by Rieche is that in the first step ethylene peroxide is formed as a monomer, or in a partially polymerized state, and is converted further as follows:



to form formaldehyde. The formation of formaldehyde proceeds in a manner analogous to the splitting of asymmetrical diphenylethylene peroxide into benzophenone and formaldehyde (Staudinger). The ethylene peroxide may react further with the other ethylene molecules, forming ethylene oxide. The formation of hydrogen peroxide may proceed in a similar manner as follows:

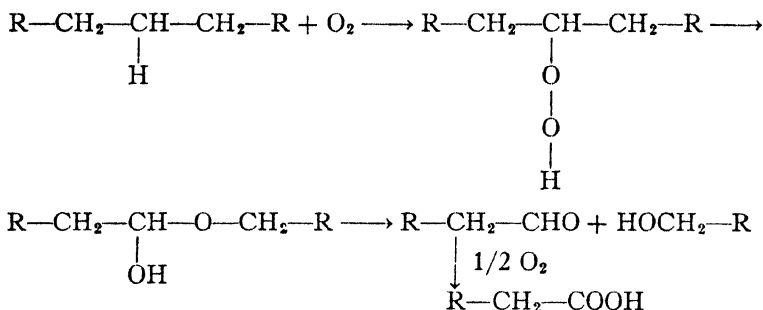


$\text{H}_2\text{O}_2 + 2\text{CH}_2\text{O}$  gives dioxymethyl peroxide,  $\text{CH}_2\text{OH—OO—CH}_2\text{OH}$ , which decomposes into  $\text{H}_2 + 2\text{HCOOH}$ . Glyoxal could originate from formaldehyde or through intermolecular disproportioning of polymer ethylene peroxide. Thus equal numbers of molecules of glycol and glyoxal originate. Lehner assumed the intermediate formation of methylene, which adds itself to ethylene, and Rieche believes that this methylene could originate from ethylene peroxide:

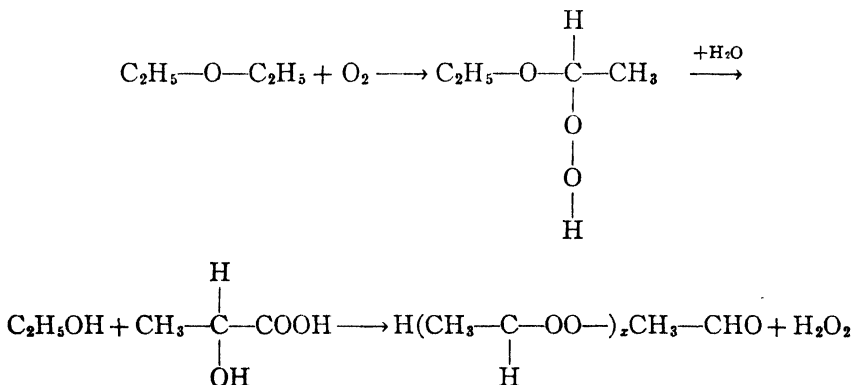


The oxidation of saturated compounds, for example, saturated acids through oxygen of the air proceeds similarly to the decomposition of acids with an even number of carbon atoms in the animal organism, and intermediate formation of  $\beta$ -keto acids. The rancidity of fats oxidized in air is based on the formation of methyl ketones originating by decarboxylation of the  $\beta$ -keto acids. The methyl ketones are further oxidized to a high molecular weight fatty acid and to formic acid. The probability of the

following reaction on the assumption of the characteristic oxidation of a paraffin hydrocarbon has been postulated.<sup>11</sup>



If a double bond formed by splitting is present in the molecule, the oxidation is supposed to take place close to the double bond. Finally, the oxidation of ethers is explained by assuming a shift of  $\text{O}_2$  between  $\text{C}-\text{H}$  with the formation of hydroperoxydiethyl ether, which gives the compounds found in auto-oxidized ether. This may be illustrated by diethyl ether as follows:



The behavior of isopropyl ether is like that of ethyl ether; dimethyl ether is oxidized with greater difficulty. Dibenzyl ether is readily oxidized.

Catalytic oxidation may be performed by using air or oxygen. The oxidation may proceed in a gaseous or a liquid medium. If the mixture of oxidizing gas and the vapor of the substance to be oxidized is passed over or through a catalyst heated to the required temperature, in case of a high temperature, there is danger of explosion. The temperature of explosion for mixtures of air with a series of organic compounds at ordinary pressure in different reaction containers (glass, platinum, silver, gold) was determined by Masson and Hamilton.<sup>33</sup> They found that in glass containers the explosion temperature was  $10-15^\circ$  lower than in metal containers, and that members of one and the same homologous series explode more readily, the higher their molecular weight. For instance, a mixture of *n*-pentane and air explodes at  $579^\circ$ , while *n*-octane and air has an explosion limit of

458°. Such determinations indicate that oxidation must be carried out 50–100° lower than the temperature corresponding to the explosion. However, in many cases, it is not possible to lower the temperature required for the oxidation process; in such cases an inert gas like nitrogen, containing only 1–5 per cent oxygen, or even carbon dioxide, is often used instead of air. It is sometimes advisable to carry out the oxidation process in two stages: (1) with a strong catalyst, but at a low temperature, and (2) over a weak catalyst, at increased temperature.

Another characteristic of an oxidation process is the intensity of oxidation. Wassiljew, Kaschtanow and Kastorskaja,<sup>45</sup> studying the kinetics of oxidation of  $\text{H}_2\text{SO}_3$  solutions and comparing the desorption and oxidation kinetics, concluded that the intensity of oxidation may be expressed by a value which is the ratio of the desorption velocity constant to the sum of the constants of the desorption and oxidation velocities. Since this value is also an objective index of the possible intensity of adsorption of  $\text{SO}_3$  gas by the solution (the desorption process of  $\text{SO}_2$  from the solution is a process parallel to that of oxidation), the kinetics of adsorption of  $\text{SO}_3$  gases by aqueous solution must depend to a great extent on the ratio of the desorption and oxidation velocities.

It has been recognized that metals of the Pt group and oxides and salts of elements that can exist in several states of oxidation, such as oxides of tungsten, vanadium, molybdenum and thorium, are most suitable as catalysts of oxidation processes. Kutzelnigg<sup>21</sup> states that the most active catalysts of oxidation are the oxides of the transition elements, which stand at the minima of the atomic volume curve. It is known that the ions of the transition elements possess the faculty of assimilating electrons (adding a complete shell containing twelve shared electrons). The transition elements are characterized by the ease with which electrons can be removed both from the outermost group of electrons and the next innermost group, with the production of bivalent and trivalent ions such as those of iron:

$\text{Fe}''$  :  $K$  level 2;  $L$  level 8;  $M$  level 14 electrons

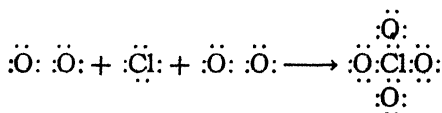
$\text{Fe}'''$  :  $K$  level 2;  $L$  level 8;  $M$  level 13 electrons

Copper resembles the transition elements in the formation of  $\text{Cu}''$  and  $\text{Cu}'$  with regard to electronic groups and therefore as regards chemical behavior.

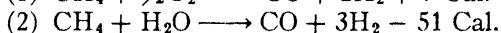
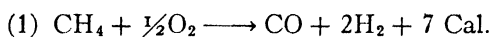
$\text{Cu}''$  :  $K$  level 2;  $L$  level 8;  $M$  level 17 electrons

$\text{Cu}'$  :  $K$  level 2;  $L$  level 8;  $M$  level 18 electrons

In this connection it must be remembered that with oxidizing agents such as  $\text{O}_2$ ,  $\text{Cl}$ , the ferric ions in general accept electrons. The oxygen atom is an acceptor of electrons, since an oxygen molecule is broken into two atoms which have only a sextet of electrons:  $\ddot{\text{O}}:\ddot{\text{O}} \longrightarrow 2:\ddot{\text{O}}$ . This is readily expanded into an octet by accepting lone pairs of electrons from other atoms, as in the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  or in the oxidation of a chloride to a perchlorate.



Among catalytic oxidation processes are some reactions of great industrial significance, which are referred to in the tables devoted to these processes. To emphasize the practical use of some of the products obtained in catalytic oxidation processes several examples are cited. Oxidation of carbon monoxide by air into carbon dioxide at ordinary temperature is very important in making gas masks. Large quantities of methane are obtained from natural gas, coke oven gas, gas from refining of crude oil, cracked gas from pressure distillation of heavy oils, as well as from carburetted water gas. This methane is a basic material of the chemical industry in the synthesis of ammonia and hydrogenation of crude oil and coal. There are two ways in which methane may be oxidized: (1) by oxidizing the carbon of methane in order to prepare hydrogen and (2) by oxidation of methane, resulting in the preparation of formaldehyde. Hydrogen is obtainable by direct splitting of methane into its elements or by catalytic conversions in the presence of oxygen or with steam.



In the case of oxidation with steam twice as much  $\text{H}_2$  is obtained as by direct splitting.

From 1 volume  $\text{CH}_4$ : 3 volumes  $\text{H}_2$

If  $\text{CO}$  to  $\text{CO}_2$  and  $\text{H}_2$ : 4 volumes  $\text{H}_2$

The heat required for the reaction is considerably greater, while the temperature of the reaction is not essentially lower. A continuous mode of operation involves heating the container with the mixture of methane and steam from the outside. Methane may be converted partly with oxygen and partly with steam, covering the energy requirements of the steam reaction by surplus heat from the oxygen reaction and making it possible to work continuously. The operation may be discontinuous when heating is periodical. Of course, methane may be converted into acetylene, a conversion product of a primarily formed radical, in case of incomplete decomposition into elements under a partial combustion with oxygen. Oxidation of methane into methanol and formaldehyde is not customary because a cheaper method is provided by manufacturing formaldehyde from methanol synthesized from  $\text{CO}$  and  $\text{H}_2$ .

Oxidation of higher hydrocarbons of the paraffin series, such as crude oil fractions, with air or oxygen into fatty acids of high molecular weight has been found of importance in the manufacture of soap. Paraffin can be converted into such acids (as was done in Germany during the World War) but paraffin is too expensive; crude and solar oils have also been used for this purpose. Fatty acids suitable for clear soaps are obtained from the oxidation products only when the reaction is controlled. To obtain an intimate contact between air and paraffin the latter can be converted into a foam. In this way a reduction in the time of oxidation from several days to a few hours, and a considerable lowering of the reaction temperature can be achieved. The product obtained consists of fatty acids, wax, alcohols and unchanged paraffin (the amount of the latter varies with con-



ditions). The paraffin and alcohols are returned for repeated oxidation. In addition to fatty acids, oxy- acids may be present, but after refining, the fatty acids are as desirable as those derived from natural fats. With respect to the mechanism of oxidation of paraffin it is assumed that oxygen attacks the hydrocarbon molecules not at the ends, but at about the middle of the carbon chains, forming large fragments. In favor of this viewpoint is first the fact that the acids obtained contain about half of the number of carbon atoms of the initial hydrocarbon, and also that only a very small amount of carboxylic acid and oxidation products of the lower members of the paraffin series is formed. Fats may be obtained from the refined fatty acids and the synthetic glycerin.

The oxidation of acetaldehyde to acetic acid represents one of the most important of the catalytic processes. Catalytic oxidation of aromatic hydrocarbons serves to prepare maleic acid, which may be used as the initial material for alicyclic and heterocyclic compounds. Oxidation of benzene into phenol is another example. Commercially, phenol is prepared from brown coal tar. The oxidation of toluene into benzaldehyde is not only the most direct reaction, but the final product has the advantage over that obtained from benzal chloride, because it is free from chlorine.

Not to be forgotten is the oxidation of naphthalene into phthalic acid anhydride which serves as an intermediate product in preparation of dyes. Likewise oxidation of anthracene into anthraquinone is important industrially for the same reason. In the United States anthraquinone is obtained synthetically from phthalic acid anhydride and benzene because extraction of anthracene from brown coal tar leaves tarry residues, which are too fragile to be used as usual for asphalt road construction. However in Germany and Russia anthracene is separated and oxidized.

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## PART III

### Catalytic Hydration and Dehydration

Addition of water to a compound as well as removing water from it may be accomplished by catalytic agents. As catalysts of both hydration and dehydration are recommended oxides of rare earths (Th, W, Ti, Zr, Mo and Cr) alone or together with promoters, such as oxides of Al, Mg, Zn and  $K_2CO_3$ . It is known that  $Al_2O_3$  greatly accelerates dehydration, but in order that it may function as a dehydrating agent it must be first heated as a hydroxide. Chromium oxide occupies an intermediate position between dehydration and hydration catalysts; in the presence of Zn it assists hydration, but prepared in a different manner it has a dehydrating action, or promotes interaction of substances with steam. Both dilute and concentrated acids serve as catalysts in hydration and dehydration processes. Alkalies are used as catalysts in dehydration of liquid systems as well as in hydrolytic processes. In selecting catalytic substances for dehydration processes more should be known about their hydration ability both in general and under specific conditions of a catalytic reaction. The hydration ability of ions composing the dehydration agent must be estimated. The measurements of electrolytic migration of ions permit the determination of the migration number of cations and, knowing the number of water molecules carried by one faraday, the hydration numbers for the ions may be calculated.<sup>1</sup>

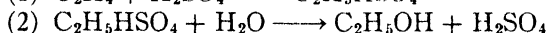
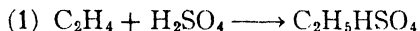
Brintzinger<sup>2</sup> determined the ion weight from the dialysis coefficient on the assumption that the hydration water does not envelop the migrating ion, but that it accumulates at a favorable place on the ions by the direction of the water dipoles. The central ions, because of their relatively high electric field, bind particularly strongly some of the water molecules in close proximity, so that these move along by diffusion and form the aqueous ions. Butler<sup>3</sup> considers the hydration energy and entropy of organic compounds; starting with Langmuir's conceptions he calculates the hydration heats  $\Delta H$  for a series of alcohols by means of theoretically determined exchange action of energies for various organic groups with water molecules. In the case of simple compounds the hydration heats are found to be additive. Likewise in chain branching certain regularities are observed, namely, that the hydration heat  $\Delta H$  decreases for each branching by

0.6–1.0 Cal. The hydration entropy  $\Delta S$  is calculated from the equation:  $\Delta S = -(\Delta F - \Delta H)/T$ , where  $\Delta F = RT \log p/N$  is the distribution coefficient between the gas and water phase; ( $p/N$ , where  $p$  is the partial pressure of the dissolved substance over water;  $N$  = mol/fraction of the dissolved substance). A linear dependence has been ascertained for the aliphatic alcohol.

The addition and withdrawal of water may occur as independent reactions as well as those accompanying other types of reactions such as condensations, oxidations, sulfonation, etc. The fundamental processes concerned with hydration are for example those dealing with hydration of acetylene or ethylene hydrocarbons. Addition of water to acetylene leads to the formation of acetaldehyde,  $C_2H_2 + H_2O \longrightarrow CH_3CHO$ , used in the production of acetic acid. At the Shawinigan plant of the Canadian Electrochemical Products Company, 500 to 600 thousand cubic feet of  $C_2H_2$  were converted daily (1919) into acetaldehyde, mercuric oxide being used as catalyst (both the raw acetylene and the catalyst are produced by electric power); the yield was 95% of the theoretical. However there are also one-step processes in which acetylene is directly converted into acetic acid or acetone (the latter requires an excess of water vapor).

Hydration of acetylene yielding acetaldehyde, may be utilized also in the production of various synthetic aliphatic compounds. On the other hand, hydration of ethylene, propylene or butylenes yields alcohols which may be produced in very large quantities on account of the abundance of these olefins. The chief sources of cheap ethylene are: (1) cracked gas (from petroleum oil subjected to pyrogenetic decomposition) and (2) coke-oven gas (from distilled brown coal).

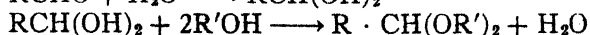
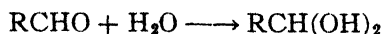
The methods used in the production of ethyl alcohol from ethylene are based on the adsorption of olefins by sulfuric acid, followed by hydration, due to dilution with water. The product obtained after distillation is the alcohol.



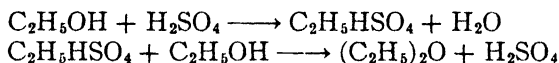
Finally there are hydration processes in which water is added, forming two independent compounds, namely, an alcohol and an acid; these are called hydrolytic processes. The conversion of starch and cellulose into simple sugars by the action of mineral acids, and the hydrolysis of fats constitute catalytic reactions of this type.

Dehydration is generally involved when removing water from alcohols as well as in the preparation of simple ethers from non-aqueous alcohols. Further products of dehydration of alcohols at high temperatures are olefins. Dehydration of acetic acid is a step in the preparation of acetic acid anhydride.

King and Mason<sup>10</sup> consider the action of  $HCl$  or  $CaCl_2$  in the formation of acetals  $[CH_3CH(OC_2H_5)_2]$  and the corresponding diethyl ether of acetaldehyde as catalytic dehydration proceeding according to the following scheme:

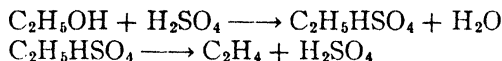


Ethyl ether is used in large amounts as an anesthetic in surgery as well as a solvent in manufacturing chemicals. A mixture of ether and alcohol has been used as a substitute for acetone as a solvent for nitrocellulose and nitroglycerin, thus being significant in the manufacture of propellant explosives. A similar mixture known as "Natalite" has been found useful as a fuel for motors. For industrial purposes ether is produced by using sulfuric acid as catalyst:



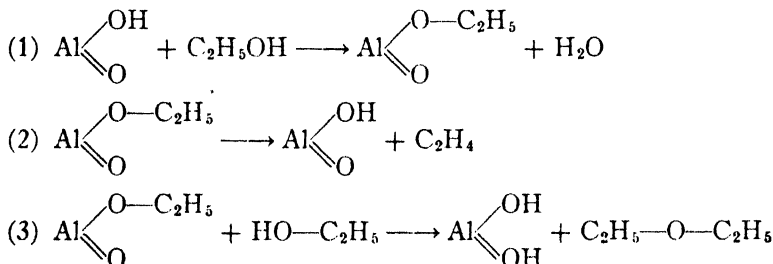
For anesthesia, ether is often sold as sulfuric ether. Methylated ether is also on the market; it is prepared from methylated or denatured alcohol.

In manufacturing olefin hydrocarbons or ethers the usual dehydrating oxides are not used; instead the catalytic action of sulfuric or phosphoric acid is applied. While ethyl alcohol changes into ethylene and water when the oxides are used at 330–450°, the reaction with  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  proceeds at 170–180°:

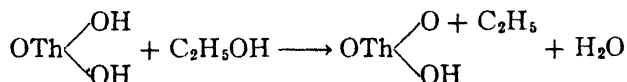


In general, dehydration of alcohol may proceed in two ways, giving either ethylene and water or ether and water. Insofar as the aliphatic alcohols are concerned, the production of ethers is decidedly the exception rather than the rule. However, Ipatieff<sup>4,5</sup> and also Sabatier and Maible<sup>12</sup> state that in dehydration with alumina at low temperatures some ether is produced in addition to ethylene. In the case of aromatic alcohols and especially phenols, dehydration results in the production of considerable amounts of diphenyl oxide or diphenyl ether. Ipatieff assumed that alumina forms a hydrate corresponding to sodium aluminate ( $\text{NaAlO}_2$ ), and deduced therefrom the course of catalytic dehydration of aliphatic alcohols with acids, forming intermediary unstable esters, decomposing readily to give the corresponding olefins.

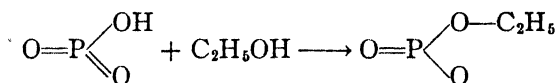
The analogy between the action of alumina and that of an acid as catalyst with respect to the alcohol Ipatieff<sup>6</sup> expressed as follows:



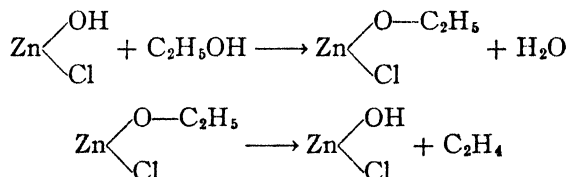
Likewise thorium oxide is supposed to exist as the hydrate,  $\text{ThO}(\text{OH})_2$ , and the dehydration proceeds as follows:



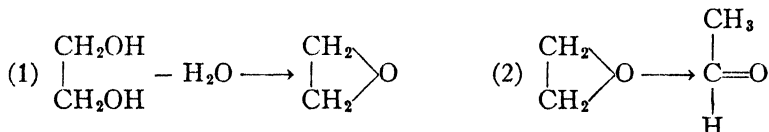
In the case of dehydration with phosphoric acid as catalyst, it is assumed that orthophosphoric acid may change into metaphosphoric acid:



In order that zinc chloride in the presence of water may act as a dehydration catalyst, it must form  $\text{ZnOHCl}$ , and the dehydration follows the scheme:



The mechanism of dehydration of polyatomic alcohols such as ethylene glycol has been studied by Ipatieff<sup>7,8</sup> and Ipatieff and Klukwin.<sup>9</sup> Ipatieff postulated two steps in the reaction: (1) ethylene glycol is dehydrated over alumina to ethylene oxide; (2) ethylene oxide as shown by Ipatieff and Leontowitch isomerizes into acetaldehyde over the same catalyst.



Furthermore the acetaldehyde polymerizes to paraldehyde in the presence of alumina. In the meantime the product contains croton aldehyde and its presence is explained by the fact that acetaldehyde undergoes aldol condensation over alumina forming acetaldol, which by losing water forms croton aldehyde, as expressed by the following equation:



A parallel running dehydration and dehydrogenation reaction was observed by Rubinstein<sup>11</sup> in the case of isoamyl alcohol, using as catalysts  $\text{Al}_2\text{O}_3$  and Ni nitrate with the addition of Ni sulfate, and applying as promoters Co, Fe, CdO and MnO or Pt on charcoal or  $\text{Al}_2\text{O}_3$ . The absolute value of the activation energy was found to be higher for all other catalysts than for Pt.

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## PART IV

## Catalytic Hydrogenation

The addition of hydrogen to substances may be promoted by a catalyst. What part the catalyst plays, in which state the hydrogen is added and how and where it attaches itself were the essential problems which investigators have tried to solve with respect to this type of catalysis. It has been recognized that molecular hydrogen would be too inert to perform the task of hydrogenation; with this fact in mind, it was assumed that various states of activation are brought about by the catalyst. That activation not only of hydrogen, but also of the substances to be hydrogenated is of importance is indicated by the fact that some substances are subjected to the action of hydrogen at a low temperature, while others using the same catalyst are at a considerably higher temperature.

With respect to the manner in which hydrogen is activated by hydrogenating substances the following possibilities have been claimed: (1) Hydrogen is dissolved physically within definite limits in the catalyst either as atom or ion. (2) With a metal, hydrogen forms unstable hydrides which give off hydrogen in the atomic state. There is a stoichiometric relationship between the metal and hydrogen, and a definite hydrogen pressure at a given temperature. (3) With metal oxides hydrogen forms unstable metal oxide hydrides. (4) Strongly deformed hydrogen molecules originate in adsorption catalysis.

To prove the validity of the first hypothesis meant showing that atomic hydrogen dissolved in metals causes hydrogenation, while hydrogen prepared in an atomic state in another way is not suitable for the purpose. Preparation of well-defined hydrogen compounds of catalytically active metals would substantiate the second hypothesis. The role played by oxygen in catalytic hydrogenation could help to provide a base for the third hypothesis. Direct experimental proof for the fourth apparently is impossible.

The fact that platinum metals are able to take up hydrogen is well known. Metals are considered to be divided into two groups: (1) those in which the gas is in true solution and in which there is no evidence of the formation of compounds, such as Fe, Ni, Co, Cu, and to a less extent Ag; and (2) those which form definite hydrides, such as rare-earth metals, Pd, Zr, Ti, Th, V, and Ta. The extent to which hydrogen is adsorbed or dissolved varies with the kind of metal, as well as conditions under which the incorporation of hydrogen takes place. Graham<sup>27</sup> observed that Pd absorbs nearly a thousand times its own volume of hydrogen at room temperature, corresponding to an atomic ratio of  $\text{Pd}_2\text{H}$ . By electrolytic charging, the ratio is about  $\text{Pd}_2\text{H}$ , but at high gas pressures the limit is rather close to  $\text{PdH}$ . The solubility decreases rapidly with rising temperature. It has been ascertained<sup>78</sup> that Ni dissolves more hydrogen than any other metal of the Fe group and that there is a very large increase in solubility at the melting point. Solubility of hydrogen in Co is very much less than in Ni, but

it increases more rapidly with temperature.<sup>70</sup> Hydrogen has been found more soluble in  $\gamma$ -than in  $\alpha$ -Fe.<sup>67</sup> It appears that in general when a metal melts, a large increase in solubility follows. Mo, Pt, and Al dissolve very small amounts of hydrogen in the solid state. In these metals dissolving is a completely reversible process and the solubility is proportional to the square root of the gas pressure. Smithells<sup>74</sup> has plotted the most probable values for the solubilities at atmospheric pressure for hydrogen in Al, Ag, Pt, and Mo, as well as in Ni, Fe, Co, and Cu, as a function of temperature (Figures 1 and 2). The solubility of hydrogen in Ag is about half that in Cu.

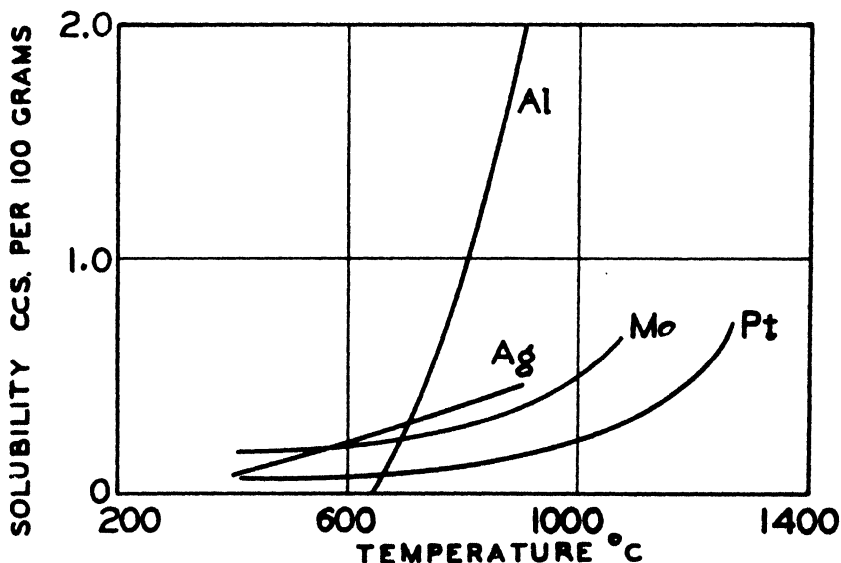


FIGURE 1.—Solubility of Hydrogen in Aluminum, Silver, Platinum and Molybdenum.

The form in which hydrogen is dissolved in a metal was first indicated by Sieverts and Jurish.<sup>71</sup> They state that the solubility of hydrogen in Pt is not proportional to pressure (according to Henry's law hydrogen should be dissolved molecularly), but is proportional to the square root of the pressure, and that hydrogen is dissolved in Pt either as atomic or as mono-atomic ions. The solubility of hydrogen in Pt does not follow any such simple law.<sup>68</sup> However, it has been expressed by an equation:  $L = A\sqrt{p} + Bp$ , according to which it is proportional to a function into which both the square root of the pressure and the linear function of the pressure enter, evidently indicating that hydrogen is dissolved as molecules and as atoms, and that the existence of a  $\text{Pt-H}_2$  compound also is not excluded.

That many gases are dissociated into atoms on metal surfaces has been proved by many investigators. Paneth<sup>58</sup> claimed that atomic hydrogen, obtained by diffusion of hydrogen through a sheet of Pt, hydrogenated S

to  $\text{H}_2\text{S}$ . However, this has been doubted because of Bach's<sup>5</sup> control results. Gauger,<sup>22</sup> from a study of the ionization potentials of hydrogen in contact with Ni, concluded that it is the atomic hydrogen which is active in the catalytic hydrogenation produced by this metal. Gauger's method was criticized by Wolfenden,<sup>90</sup> but still he arrived at the same conclusion that much of the hydrogen is present as atoms at the surface.

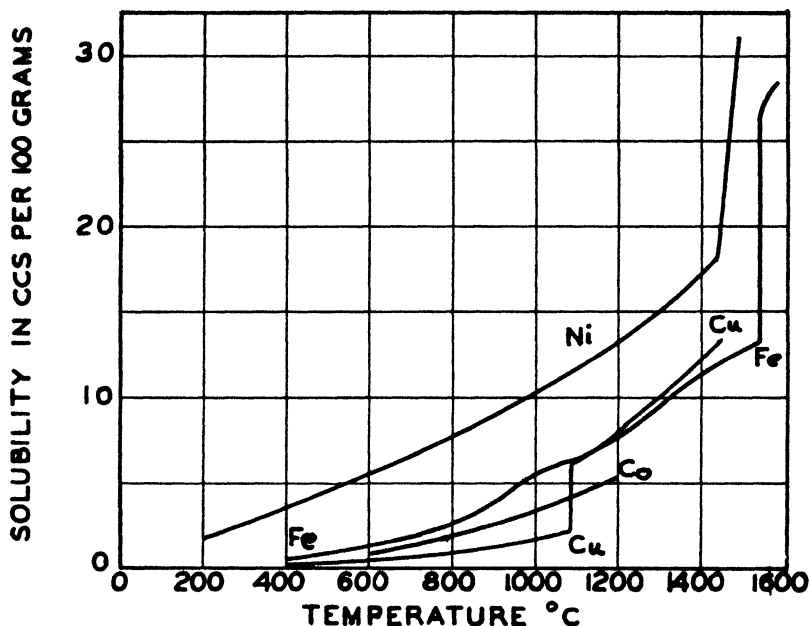
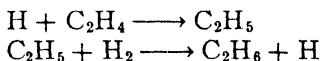


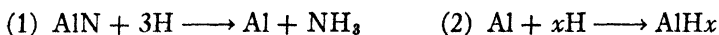
FIGURE 2.—Solubility of Hydrogen in Nickel, Iron, Cobalt and Copper.

Taylor<sup>79</sup> suggested that if hydrogenation of ethylene is carried out by atomic hydrogen according to



then the introduction of a free ethyl radical into a mixture of hydrogen and ethylene should cause the hydrogenation of the ethylene also. Later this mechanism was abandoned by the writer.

Recently Koboseff, Jerofejew and Savina,<sup>43</sup> investigating the hydrogenation of Al nitride with hydrogen obtained by electric discharge and with mixtures of  $\text{N}_2$  and  $\text{H}_2$  in a ratio 1 : 3, found that the process is especially energetic with atomic hydrogen, its presence being proved spectroscopically. The reaction proceeds as follows:



Hydrogenation of Al nitride through active H proceeds up to liberation of  $\text{NH}_3$  in contrast to the behavior of molecular  $\text{H}_2$  which does not hydrogenate. It is believed that this reaction may serve as an indicator for atomic hy-



drogen. After the completion of the reaction no drop in the N content in the nitride takes place, but rather an increase for both cases of pure hydrogen and N—H mixtures. The hydrogenation velocity depends very little on time and on the percentage content of hydrogenated Al nitride. This reaction is of importance insofar as metallic Al may be obtained from a low percentage of AlN with liberation of  $\text{NH}_3$ .

Kistiakowski<sup>42</sup> found individual atoms of nitrogen and hydrogen adsorption on a number of metals. Diffraction patterns<sup>12</sup> from a single crystal

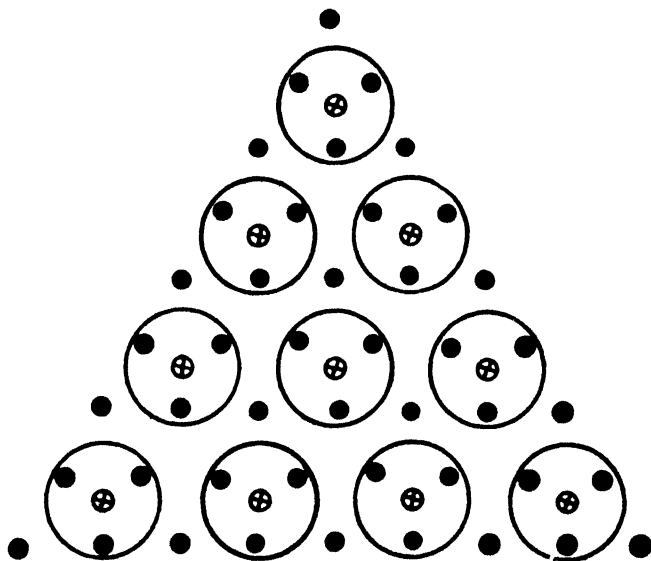


FIGURE 3.—Arrangement of Hydrogen Atoms Adsorbed on a Nickel Surface.

⊕ Hydrogen Atoms.  
● Nickel Atoms.

of nickel on which hydrogen had been adsorbed (Figure 3) revealed that hydrogen molecules formed a lattice similar to that of the underlying nickel, but with twice the atomic spacing. The gas molecules cover about 3 nickel atoms. When nickel is heated to  $100^\circ$  the adsorbed gas is driven off and the normal nickel pattern is reestablished.

Hydrogen and oxygen are dissociated on tungsten and may come off as free atoms if the metal is sufficiently heated. The main difference between the action of hydrogen and oxygen on the tungsten filament appears to be that the attachment of the single atoms to the filament is far stronger for oxygen than for hydrogen; this is due to the greater chemical affinity of tungsten for oxygen. "Active" hydrogen prepared by electrical discharge by Bonhoeffer<sup>7</sup> and used to hydrogenate oleic and stearic acids was assumed to consist of neutral atoms. Schmidt<sup>65</sup> in agreement with Wilson<sup>89</sup> and Richardson<sup>69</sup> assumed that on a metal a dissociation into ions takes place and that hydrogen ions cause catalytic hydrogenation. Schmidt thought

that Bonhoeffer's hydrogen atoms, rendered active by the hydrogenation catalysts Pt, Ni, and Cu, are at once converted into inert molecular hydrogen, and that  $2\text{H} = \text{H}_2$ , the reaction that removes the active hydrogen, is strongly accelerated by metals. Schmidt sought support for his viewpoint in Thomas'<sup>82</sup> statement that from Pt charged on one side by hydrogen and on the other by ethylene a gas chain may be obtained, in which the hydrogen electrode is the negative pole and the ethylene electrode is the positive, ethylene behaving as a negative ion and the whole reaction being ionic.

If unstable metal hydrides are assumed to be intermediate products of hydrogenation, then the metals in question should readily give the hydrides on treatment with hydrogen. Some investigators succeeded in preparing the latter. Schlenk and Weichselfelder<sup>64</sup> claimed the preparation of  $\text{NiH}_2$  by introducing hydrogen into an ether solution of colloidal Ni. Hydrides of Co, Fe, and even Cr (although not active in the transfer of  $\text{H}_2$ ) were also obtained.<sup>86</sup> Gaydon and Pearce<sup>23</sup> established spectroscopically the existence of nickel hydride ( $\text{NiH}$ ). A hydride of copper ( $\text{CuH}$ ) has been prepared by a chemical method,<sup>69</sup> as well as by the action of atomic hydrogen on an activated copper surface.<sup>53</sup>

It has been postulated by Ipatieff<sup>37</sup> that in hydrogenation  $\text{NiO}$ , not Ni, is the catalyzing agent. Willstätter and Waldschmidt-Leitz<sup>88</sup> found that shaking Pt black, freed from oxygen, with hydrogen for hours made it inactive for any catalytic hydrogenation, even for the hydrogenation of an olefinic double bond. However, after treatment with oxygen the catalyst regained its original activity. It seems likely that hydrogenation requires the presence of oxygen. The coexistence of hydrogen and oxygen without a rapid formation of water has been ascertained. Hydrogen and oxygen may be adsorbed in various pores and the diffusion toward each other is a slow process. Willstätter considered the possibility of a Pt peroxide,

Pt  $\begin{matrix} \diagup \text{O} \\ \diagdown \text{O} \end{matrix}$  able to form compounds of the formula:  $\begin{matrix} \text{H} \\ \diagup \\ \text{H} \end{matrix} \text{Pt} \begin{matrix} \diagup \text{O} \\ \diagdown \text{O} \end{matrix}$  which may add water or acetic acid and function as intermediate compounds in catalytic hydrogenation.

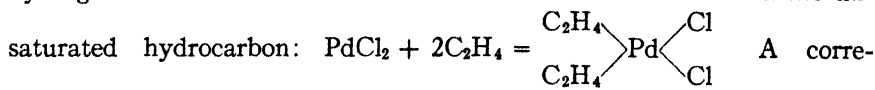
Bonhoeffer<sup>7</sup> and Wood<sup>91</sup> ascribed a different role to oxygen. According to these investigators, the active atomic hydrogen may combine just as well with a second hydrogen atom ( $\text{H} + \text{H} = \text{H}_2$ ) as with the compound to be hydrogenated. Oxygen catalyzes negatively the first reaction and therefore hydrogenation of the reacting compounds takes place. How the formation of hydrogen molecules is retarded is not revealed. The influence of oxygen upon the velocity and course of hydrogenation with Pt black has been proved, but still the presence of oxygen cannot be considered essential in all cases of hydrogenation. Skita<sup>72</sup> has shown that in catalytic hydrogenation with colloidal Pt the presence of oxygen is not required for carrying out hydrogenation. At temperatures above  $40^\circ$ , platinum superoxide is not the carrier of catalytic action. While platinum black completely lost its catalytic activity after 30 hours of shaking with hydrogen, Skita's platinum hydrosol maintained its activity after the same treatment. How-

ever, Paal proved the presence of small amounts of oxygen (up to 4 per cent) in his preparations of colloidal metals.

The part of oxygen in catalytic hydrogenation has been interpreted by Kuhn<sup>44, 45</sup> in the sense that the activation of hydrogenating catalysts by oxygen is not the result of a depoisoning effect, as assumed by Bodenstein, but the result of poisoning of Pt in the recombination of hydrogen atoms, as postulated by Wood.<sup>91</sup> Bodenstein's assumption is not confirmed by the loss in the activity of the catalyst with increasing discharge of gas in a high vacuum and its regeneration by charging with O<sub>2</sub>. Kuhn explains the activation of H<sub>2</sub> by Pt—O compounds by the fact that the metal giving off electrons to the O<sub>2</sub> makes the H<sub>2</sub> molecules labile by withdrawal of electrons, and thus facilitates hydrogenation or hydrogen addition to unsaturated compounds. The density of covering with O<sub>2</sub> determines whether the acting electric forces will change in the intermediate layer and thus influence the stability of hydrogen molecules. Roberts,<sup>60</sup> studying the effect of admitting oxygen to a surface already covered with hydrogen, found that the oxygen is adsorbed, but for each molecule adsorbed a molecule of hydrogen is driven off. It is a slow process and resembles the normal process of activated adsorption.

The type of hydrogen activation proposed in the Raschig-Bodenstein<sup>6</sup> hypothesis considers that deformed molecules are capable of reacting in catalytic hydrogenation. The fact that, through the addition of activated hydrogen, *cis* and *trans* compounds are alternately formed, has been interpreted by Kuhn in the sense that hydrogen may be activated to an H atom, an H<sup>+</sup> ion and an H<sub>2</sub> molecule, and that every kind of activation corresponds to a special catalyst. Hückel thought the explanation was improbable and that activation of compounds to be hydrogenated is involved. Hückel's assumption was to the effect that, for various catalysts in acid and neutral solutions and at various temperatures, the molecules of unsaturated compounds are deformed in a different manner, so that the form of the molecule is favorable now for the *cis* addition of hydrogen and then for the *trans* addition.

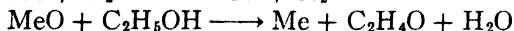
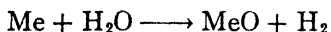
Wieland postulated loose addition compounds between the metal hydride and the unsaturated compound being hydrogenated:  $\text{PdH}_2 + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_6 + \text{Pd}$ . Another possible mechanism is that activated hydrogen is attached to an addition compound between Pd and the unsaturated compound undergoing hydrogenation rather than the unsaturated compounds accumulating at Pd—H<sub>2</sub>. Addition compound formation previous to hydrogenation has been assumed<sup>73</sup> between a metal chloride and the un-



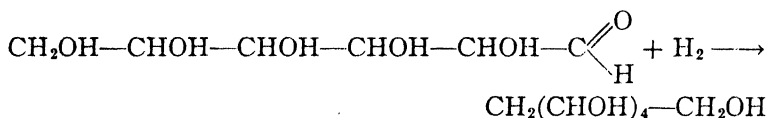
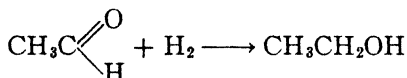
sponding compound has been prepared from isophoron. Through hydrogen the chlorine is taken out and the resulting addition compound between the unsaturated compound and the metal in a molecular distribution is attacked readily by the surrounding hydrogen and decomposed.

Different types of mechanisms by which hydrogenation catalysis occurs have been suggested by many investigators. According to Ipatieff

the mechanism for hydrogenation and dehydrogenation is one in which the metal catalysts form metal oxides with the aid of water, whereby hydrogen is given off, and the oxides then oxidize the organic compounds by removing their  $H_2$ .



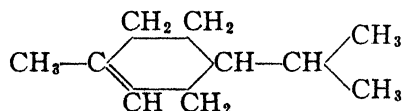
In some cases the metal takes hydrogen from the organic compounds with the formation of unstable metal hydrides, which give off hydrogen, the metal being regenerated. Organic compounds containing oxygen such as aldehydes, ketones and others, are hydrogenated into alcohols according to the scheme:



Catalysts used in hydrogenation processes may be considered to function in the sense of causing a saturation of the free bonds by the active hydrogen atoms. Saturation of unsaturated hydrocarbons having straight chains occurs without difficulty. Unsaturated chains of a cyclic nucleus will be difficult to hydrogenate. Hydrogenation of unsaturated fats, for instance, occurs with great ease when unsaturates of acyclic groups are present; but the presence of small amounts of cyclic compounds, such as benzene, toluene, naphthalene, and phenol will, on the contrary, weaken the hydrogenation process.

Almost all organic compounds containing ethylenic or acetylenic linkages, many aldehydes and ketones, as well as the benzenoid ring system of many aromatic compounds undergo addition of hydrogen in the presence of catalysts and under suitable conditions of temperature and pressure. Catalysts suitable for hydrogenation are, in nearly all cases, metal compounds occurring in various stages of valence and are readily converted into one another.

Sabatier and Senderens<sup>61</sup> stated that in hydrogenating terpenes, for example limonene, over reduced Cu, the limonene adds two hydrogens to the double bond in the aliphatic side chain, yielding menthane,  $(C_{10}H_{18})$ , a hydrocarbon of the structure:



This hydrocarbon, when subjected to a second hydrogenation, adds two hydrogen atoms to the double bond in the nucleus and a menthane, identical with the hydrocarbon formed over reduced Ni (Sabatier and Senderens) and over Pt black (Vavon), is obtained under ordinary pressure. Ipatieff

states that hydrogenation of limonene is accelerated by CuO rather than by reduced Cu. In the presence of reduced Cu, hydrogenation of pinene proceeds in the same way as in the presence of CuO, except that at 280–290° a product of the composition  $C_{10}H_{18}$  is obtained, whereas with CuO, at the same temperature,  $C_{10}H_{20}$  is formed. Only at 300° does the hydrogenation of pinene over reduced Cu proceed further. In order to obtain  $C_{10}H_{20}$ , it is necessary to hydrogenate twice. With NiO, the addition of hydrogen to pinene under pressure proceeds more rapidly and at a lower temperature than over CuO, and menthane is formed.

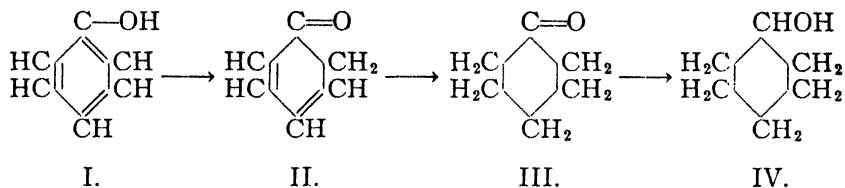
According to Ipatieff<sup>38, 52</sup> hydrogenation of pinene in the presence of a catalyst involves the following three reactions:

- (1) Hydrogenation of the double bond in the ring.
- (2) Opening of the tetramethylene ring, with simultaneous hydrogenation.
- (3) Isomerization of pinene into dipentene, followed by the addition of one or two molecules of hydrogen to the latter.

The final result of the process may be the formation of dihydropinene or of dihydrodipentene by addition of one molecule of hydrogen, or of menthane by the addition of two molecules of hydrogen. The relative amounts of the two isomers of which menthane consists depend upon the manner in which the cyclobutane ring opens; that is, the methyl group may be either *ortho* or *para* with respect to the isopropyl group. The presence of both isomers is indicated by the wide range of the boiling points of menthane, while menthane from hydrogenated limonene is uniform and distills at 169–170°.

When hydrogenating phenols containing an unsaturated side chain over Ni, Ipatieff<sup>38</sup> observed a simultaneous saturation of both the side chain and the nucleus. CuO promotes hydrogenation of unsaturated side chains as well as of the nuclear double bonds at 290–300°, but under these conditions the aromatic ring does not undergo hydrogenation. Hydrogenation of the benzene ring takes place in the presence of Ni under high pressure. Ipatieff, hydrogenating various aromatic compounds at high temperature (450°) and high pressure, showed that the isomerization of 6-membered rings into 5-membered rings is a common occurrence in the presence of catalysts. For example, hydrogenation of phenol with mixed NiO— $Al_2O_3$  catalyst at 450° and under initial hydrogen pressure of 100 atm. produces up to 90 per cent by weight of a mixture of cyclohexane and methyl cyclopentane. The formation of ketone from phenol at a low temperature Ipatieff interprets as follows: under the influence of hydrogen the phenol is rearranged from its enolic form (I) to the unstable ketonic form (II), then adds four atoms of hydrogen at the places where double bonds are present; thus cyclohexanone (III) is obtained as the first product of the reaction; the excess of hydrogen reduces it to the alcohol—cyclohexanol (IV). Confirmation of this is sought in the fact that at a high temperature the ketone is not obtained, and therefore cyclohexanone is not the decomposition product of cyclohexanone but the primary product of the reaction. Complete reduction of the ketone (method of preparation of cyclohexanol)

requires a higher temperature. The scheme for the entire process is given by Ipatieff as follows:



NiO has been found to be a more effective catalyst for the hydrogenation of phenol into cyclohexanol as well as in hydrogenation of acetone to isopropyl alcohol. Ipatieff's investigations on hydrogenation of ketones to form alcohols proved that one and the same catalyst may be suited both for the decomposition of alcohols into ketones and for the reduction of ketones into alcohols, in other words indicating a reversibility of the catalytic reaction. Such a catalyst is iron.<sup>39</sup> This reversibility was studied also in the case of hydrogenation of acetone over CuO and Zn dust as catalysts. By heating methyl alcohol with an excess of hydrogen at high pressure and temperature over reduced nickel, it was shown<sup>38, 52</sup> that instead of obtaining methane and water the latter oxidized the methane to carbon dioxide, indicating that the reaction is reversible. This is shown by the equations:



The second reaction is also reversible under high pressure in the presence of reduced metal and water. Water is an oxidizing agent under pressure and at comparatively low temperatures, as shown by Ipatieff's experiments on the displacement of metals by hydrogen.

Zelinsky<sup>92</sup> attempted to prove that the intermediate products in hydrogenation of aromatic hydrocarbons and those obtained by dehydrogenation of their perhydrides over catalysts Pd and Pt, although not found, could be formed as products of incomplete hydrogenation. The reversibility of the reaction prevents their separation at the time of formation. An oxidation-reduction mechanism has been postulated. The heat evolved in hydrogenation and dehydrogenation processes is small, and small changes in temperature are sufficient to reverse the reaction. A saturated hydrocarbon such as cyclohexane, according to its chemical nature, is a labile system and is rendered unstable by contacting definite catalysts. Pd freed from O<sub>2</sub> and H<sub>2</sub>, such as ordinary Pd black, causes an irreversible catalysis of cyclohexane at 90°. The function of Pd black and similar catalysts is to produce an acceleration of the process, whereby the reaction C<sub>6</sub>H<sub>6</sub> + 3H<sub>2</sub> to C<sub>6</sub>H<sub>12</sub> is shifted to the right. However, at a temperature above 150° the reaction proceeds in the reverse direction.

According to Vavon<sup>84</sup> the total velocity of a hydrogenation reaction depends on the following processes: (1) the charge of the catalyst with hydrogen; (2) diffusion of the reacting compound (C) toward the catalyst, and (3) diffusion of the compound (C) + H<sub>2</sub> from the surface of the catalyst into the solvent. In case a mixture of two compounds, C and C', is hydrogenated, the distribution of H<sub>2</sub> between them depends on the velocity of

the second process. This velocity has been found high for maleic acid and small for pinene, and therefore maleic acid is hydrogenated first. The total velocity in this case depends on the backward diffusion of the hydrogenation product.

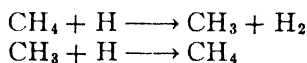
Considering catalytic hydrogenations of carbon compounds as ionic reactions, Schmidt<sup>65</sup> believes elements act in a metallic form and not as oxides or other compounds. Typical catalysts of hydrogenation belong to a group deduced from the Staigmüller<sup>77</sup> arrangement of the periodic system. These catalysts form labile compounds with  $H_2$  and their content in hydrogen is given by the formula:  $L = R\sqrt{p}$ , provided the temperature is constant. The square root relationship indicates the dissociation of  $H_2$  in the dissolving process. For elements in which this ionization takes place, it is assumed that the radius and the charge of the ions are suitable. Thus, in hydrogenating ethylene ( $C_2H_4 + H_2 \longrightarrow C_2H_6$ ) over powdered metals (Zn, Ni, Co, Fe), Schmidt<sup>65</sup> presumes that all of them are good catalysts under favorable conditions because of the smallness of the radii of their ions, while Ag and Au should prove unsuitable for catalyzing the reaction on account of their large ionic radii. The catalytic action of Pt in hydrogenation should be equal to zero. Schmidt's investigation on the reactivity of Ni in hydrogenation processes seems to indicate that surface development may be estimated from the dissolution velocity of powdered metals in acids. Hydrogen adsorbed by the catalyst is measured by pumping off and burning the remaining part. In the case of Ni, the portion of hydrogen which may be pumped off increases with increasing temperature, and conforms well to the square root law. From the constants in the relationship of the amount of hydrogen expressed in mg./g. of Ni to the relative surface of the equally pretreated metal, Schmidt draws the conclusion that adsorbed hydrogen at 20° and 760 mm. pressure is present chiefly at or in the surface, and that the hydrogen adsorption is proportional to the surface of the Ni powder. Thus the reactivity of the Ni powder, measured by half the time in which a given amount of the ethyl ester of cinnamic acid is reduced by one gram of Ni in an atmosphere of hydrogen, is stated to be proportional to the surface magnitude and the hydrogen adsorption. Additions to Ni may influence both the adsorption and the reactivity. In general, Ni is classed as a "violent" hydrogenation catalyst in the sense that it hydrogenates to complete saturation. This is the case with hydrocarbons of the olefin and acetylene series, as well as other types. However, I. G. Farbenindustrie A.-G.<sup>35</sup> found that it is possible to hydrogenate acetylene only to the olefin stage over a Ni catalyst.

In a study of hydrogenation processes of acetylene over Pd catalyst in the cold, Bourguet<sup>19</sup> proposed differentiating three phases in the course of the reaction: (1) the formation of a complex ( $Pd_nH_2$ ); (2) the formation of a new complex  $Pd_nH_2-C_2H_2$  derivative, and (3) the decomposition of the latter to  $Pd_n$  and an ethylene derivative, whereby the cycle is renewed.

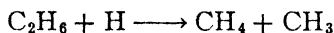
Fritzman<sup>19</sup> ascribes the catalytic activity of the Pd hydride to the metal, and to the activation of hydrogen caused by absorption or adsorption at the metal by the formation of a metastable hydrogen isomer, which is a modification having a different energy content and capable of forming

intermediate labile compounds with the metal. This conception attributes great significance to hydrogen adsorption in reduction catalysis. By diffusion or occlusion, which in the case of a metal corresponds to a dissolution, the hydrogen is brought into an atomic state as indicated by the fact that the solubility is proportional to  $\sqrt{D}$ . However, Fritzman assumes that simultaneously with the dissolution effect a solvation process takes place, which leads to the formation of unstable compounds between the metal-solvent and the hydrogen gas (hydride formation). In the case of palladium, the metal exhibits unusual valences ( $\text{Pd}_2\text{H}$ ,  $\text{Pd}_3\text{H}_2$ ) which is explained by the transition of hydrogen into the metallic state. The metallic hydrides  $\text{Me}_x\text{H}_y$  are believed to be analogous to organo-metallic compounds, and the latter may be considered as derivatives of hydrides in which the H atom has been replaced by a radical.

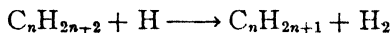
It is the decomposition of these compounds, as well as their addition ability with respect to radicals and H atoms, that causes their great significance in synthesis and reduction catalysis. Moreover, Fritzman believes that the presence of oxygen or other ingredients in the system  $\text{H}_2$ —Pd may cause surface activation of the metal, polarization phenomena, etc. Depending upon conditions, the state of the hydrogen in the  $\text{H}_2$ —Pd system may change, as well as the relative amounts of the forms, *i.e.*, atoms (*in statu nascendi*, metastable), protons, or ions. Bonhoeffer and Harteck,<sup>8</sup> studying the effect of atomic hydrogen on methane, ascertained that although the hydrogen was unaffected it nevertheless catalyzed the recombination of hydrogen atoms as follows:



The reaction of atomic hydrogen with ethane produced methane, ethylene and acetylene. The mechanism suggested for the methane formation was:



The dehydrogenation was thought to occur through the radical formation:



They found that atomic hydrogen causes a rupture of the benzene ring, forming methane, ethylene, and ethane at temperatures of about 300°. A free radical formation has been postulated as a mechanism for these reactions, the radicals being produced by scission of the C—C and C—H bonds under the influence of atomic hydrogen. Spectroscopic evidence for the momentary independent existence during the reaction of such radicals as  $\text{CH}_3\cdot$ ,  $\text{CH}_2\cdot$ , and  $\text{CH}\cdot$ , was obtained.

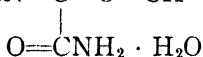
Hydrogenation of cyanogen to oxamide in the presence of acetaldehyde as catalyst, first described by Liebig,<sup>49</sup> has been interpreted, with respect to the mechanism of the reaction, by Langenbeck,<sup>47</sup> who considers it a catalysis based on an intermediate reaction of the enolic form of the aldehyde with cyanogen. Propionaldehyde undergoes the same action. The hydrogenation of cyanogen by acetaldehyde catalyst results in the forma-



tion of an intermediate product: 
$$\begin{array}{c} \text{HN}=\text{C}-\text{O}-\text{CH}=\text{CH}_2 \\ | \\ \text{H}_2\text{N}-\text{C}=\text{O} \end{array}$$
 which, when

heated with water or treated with alkalis, decomposes into 
$$\begin{array}{c} \text{H}_2\text{N}-\text{C}=\text{O} \\ | \\ \text{H}_2\text{N}-\text{C}=\text{O} \end{array}$$
 and acetaldehyde,  $\text{CH}_3\text{CHO}$ . This intermediate product is not the first step in the chemical exchange action between the reacting molecules and the catalyst. According to Langenbeck,<sup>48</sup> 
$$\begin{array}{c} \text{N}=\text{C} \\ | \\ \text{N}=\text{C} \end{array}$$
 and the  $2\text{CH}_2=\text{CHOH}$

forms first the unstable addition product 
$$\begin{array}{c} \text{HN}=\text{C}-\text{OCH}=\text{CH}_2 \\ | \\ \text{HN}=\text{C}-\text{OCH}=\text{CH}_2 \end{array}$$
, the acetaldehyde reacting in the form of the isomeric vinyl alcohol; the addition product decomposes with splitting off of  $\text{CH}_3\text{CHO}$  and the formation of  $\text{HN}=\text{C}-\text{O}-\text{CH}=\text{CH}_2$ , mentioned above.



A consecutive addition of two protons, instead of a simultaneous addition of two neutral atoms of hydrogen, was proposed by Burton and Ingold<sup>11</sup> as a mechanism for the hydrogenation of olefins. The reducing agent, such as a metal and an acid, is assumed to react in 3 stages:

(1) A proton from the acid is added to an activated double bond to form a positively charged ion:  $\text{H}^+ + \text{CH}_2=\text{CH}_2 \longrightarrow \text{H} \cdot \text{CH}_2-\text{CH}_2^+$ .

(2) The organic cation acquires two electrons from the metal and is converted into an anion:  $\text{H} \cdot \text{CH}_2-\text{CH}_2^+ + \text{Zn} \longrightarrow \text{Zn}^{++} + \text{HCH}_2-\text{CH}_2^-$ .

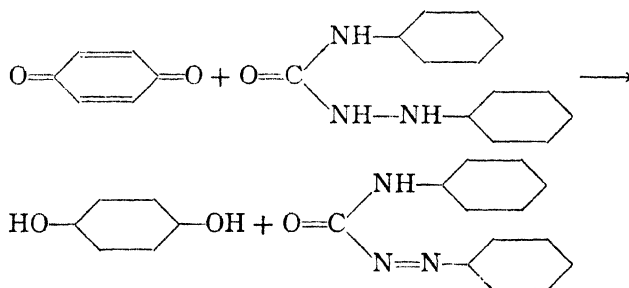
(3) The resulting anion,  $\text{HCH}_2-\text{CH}_2^-$ , adds on a second proton and becomes a neutral saturated compound:  $\text{HCH}_2-\text{CH}_2^- + \text{H}^+ \longrightarrow \text{H} \cdot \text{CH}_2-\text{CH}_2\text{H}$ .

Reduction of aldehydes and ketones, nitro- and nitroso- compounds, azo- compounds, etc., has been explained by this mechanism. In the catalytic hydrogenation of olefinic compounds the state of the catalyst greatly affects the proportion of the products.<sup>16</sup> It has been ascertained that the course of hydrogenation of sorbic acid over an aged catalyst is very different from that previously observed. In the hydrogenation of sorbic acid all the conjugated acid disappears before the three isomeric ethylenic acids are attacked. The relative yield in tetrahydrogenated  $\alpha\beta$ ,  $\alpha\delta$ , and  $\gamma\delta$  dehydrogenated compounds depends not only on the constant of the olefin molecule, but also on the state of the catalyst. Furthermore the relation of adsorption to hydrogenation catalysis of ethylene has been emphasized by Harker.<sup>28</sup> In the hydrogenation of ethylene with Cu supported on diatomaceous earth as a catalyst, both adsorbed  $\text{H}_2$  and activated Cu centers were recognized to be essential for catalysis. Adsorption of ethylene retards the activity of the catalyst. It is postulated that the activated  $\text{H}_2$  molecules attach themselves to the active Cu centers, forming a complex readily

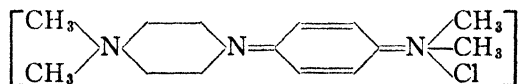
decomposed by  $C_2H_4$ , producing  $C_2H_6$ . A certain mobility is necessary in order that the activated  $H_2$  molecules may attach themselves to the active Cu centers. The adsorption of other gases such as  $C_2H_4$  and  $C_2H_6$  impedes this movement across the surface, and this results in retarding the reaction rate and sometimes in complete inhibition of the reaction.

Schuster<sup>66</sup> found that measurements of the hydrogenation velocity of an adsorbed ethylene layer are easily reproducible and that they may serve to determine the hydrogenation activity of various catalysts. The velocity constant depends on the conditions under which gas has been removed from the carbon. A carbon freed from gas at  $300^\circ$  possesses no hydrogenation activity. Whether a carrier is suitable or not as a catalyst is determined by the rate of ethylene adsorption to that of ethane. It has been shown also that increasing amounts of Ni brought into contact cause the velocity constant to increase linearly with the Ni content, while adsorbed Fe increases the activity very little and acts less strongly than incorporated iron. In addition it is stated that higher unsaturated hydrocarbons are hydrogenated more slowly than the lower hydrocarbons.

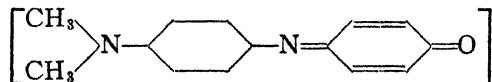
Akabori and Suzuki,<sup>4</sup> applying Wieland's theory of hydrogen activity, assume a catalytic transference of hydrogen within organic compounds. In the study of the kinetics and chemism of the hydrogenation of organic compounds through other organic substances, such as the hydrogenation of various substituted quinones by diphenylsemicarbazide,



it was found that the addition of certain dyestuffs had a pronounced catalytic effect. Bindchedler's green proved to be especially effective



and phenol blue:



as well as the related compound, *i.e.*, indophenol, tetramethylphenylene-diamine, dimethylphenylene, diamine and dimethylaminophenol.<sup>62</sup>

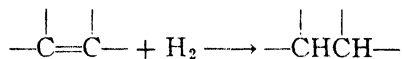
Wiesner<sup>87</sup> proved that, like isatine in other hydrogenation-dehydrogenation reactions, dyestuffs act catalytically in the sense of transporting

hydrogen. The mechanism of hydrogenation catalysis with sodium hydride as catalyst has been interpreted as one involving the formation of intermediate compounds.<sup>33</sup> It has been ascertained that NaH favors catalytically the hydrogenation of substances like aromatic hydrocarbons and substances with double bonds under high pressure, and finally those substances in which the same action is achieved by using NaNH<sub>2</sub>. The catalytic action of NaH is greatest at a temperature at which sodium adsorbs hydrogen most rapidly (in an autoclave), while at higher temperatures NaH changes into a cracking catalyst with the formation of dibenzyl, polystyrol, etc. In another instance<sup>25, 34</sup> the mechanism of hydrogenation catalysis with NaH is described and the catalytic activity of NaH is again limited to parts of the molecule which add the H<sub>2</sub>.

The mechanism of hydrogenation catalysis has been formulated by Bourguet, Gredy, Coustel and Belis<sup>10</sup> as follows: the hydrogenation catalyst Pd takes up H<sub>2</sub> in order to form a film Pd<sub>n</sub>H<sub>2</sub>, which with a surface arrangement H · Pd · H faces the organic phase; the substance to be reduced is adsorbed on this film at the point of attack and can be set free from it in an activated state. In this state it may either combine with H<sub>2</sub> or suffer deactivation or stereomutation.

Kindler and Peschke<sup>40</sup> found that while with Pd and elemental hydrogen benzal and  $\beta$ -phenylethylidene,  $\beta$ -phenylethylamine are hydrogenated smoothly at the C=N double bond, tetralene passes through the intermediate phase of hydrogenated compounds leading to the formation of ammonia, toluene and ethyl benzene, as well as ammonia and two molecules of ethyl benzene. Likewise  $\beta$ -phenylethylamine forms ethyl benzene, and benzylamine and tribenzylamine are deaminated to toluene. With boiling tetralene and palladium the hydrogenation of the double bond occurred smoothly for cinnamic acid nitrile, the 4-chlorocinnamic acid and cinnamic acid nitrile. Even for furacrylic acid the reduction proceeds selectively up to fura-propionic acid, while with palladium and elemental hydrogen (1 mol) side products are obtained in excess.

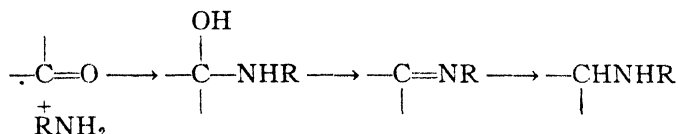
Adkins in his book<sup>3</sup> gives illustrations of the manner in which hydrogenation of various linkages takes place. For instance hydrogenation of the alkene linkages, considered the most readily hydrogenated functional group (alkene linkages are rapidly saturated at a low temperature), is expressed as follows:



(the Raney Ni catalyst requires 100° and 100 atm. pressure; Cu—Cr oxide, a temperature of 100–175°). The carbonyl group in aldehydes or ketones is rapidly hydrogenated under comparatively mild conditions, such as room temperature and 2–3 atmospheres' pressure, using Raney's Ni. Under this condition the carbonyl group hydrogenates to form alcohols: —C=

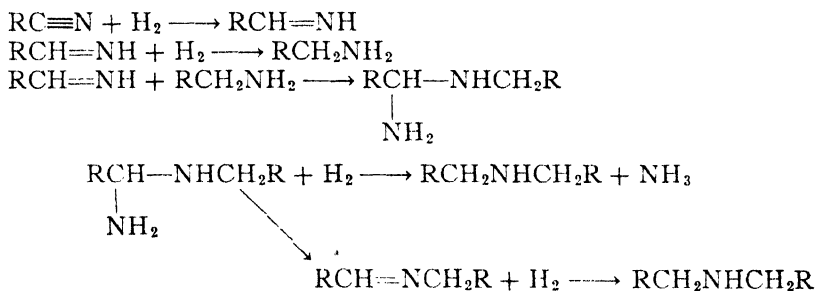
$O + H_2 \longrightarrow \begin{array}{c} | \\ -CHOH \\ | \end{array}$ ; at higher temperatures and pressures it is hydrogenated to form carbinols. Hydrogenation of carbonyl compounds in the

presence of ammonia or amines to form secondary amines proceeds as follows:



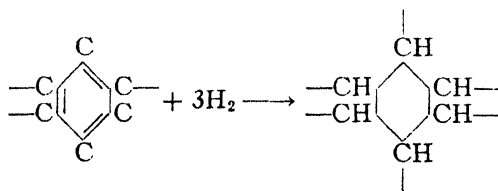
Imines, such as benzaldehyde (in alcohol) and piperidine, hydrogenate very readily to form phenylbenzylamine and *n*-butylpiperidine, respectively. The temperature required for Raney's Ni is below 80°, while that estimated for Cu—Cr oxide catalyst is 175°.

The hydrogenation of cyanides over Ni takes place at 100–150° whereby primary amines are formed:  $\text{KCN} + 2\text{H}_2 \longrightarrow \text{KCH}_2\text{NH}_2$ . Hydrogenation of cyanides and oximes with side reactions leads to the formation of secondary amines as a result of an interaction between an imine and a primary amine:



In case the formation of secondary amines is to be avoided, the hydrogenation must proceed as rapidly as possible, using a halogen-free cyanide, a high ratio of the catalyst, and sufficiently high temperature and pressure.

For hydrogenation of the benzene nucleus more drastic physical conditions are required than for that of the alkene, carbonyl, cyano- and imino-groups. Rather rapid hydrogenation proceeds over Ni at 125° and 100 atmospheres. The scheme of hydrogenation is as follows:



Ssachanen and Tilitschejew,<sup>76</sup> studying pressure hydrogenation of crude oil, discuss the mechanism of hydrogenation reactions. In pressure hydrogenation as in the case of cracking, decomposition and condensation processes take place side by side. At higher temperatures (400–500°) splitting reactions enter into the hydrogenation process which leads to a rearrangement in the condensed ring hydrocarbons. Phenanthrene and anthracene

give naphthalene and finally benzene derivatives at 450–500° and at high pressure.

Varga and Makray<sup>83</sup> state that in pressure hydrogenation of cracking benzene the unsaturated compounds are converted not only into aliphatic, but also into aromatic and hydroaromatic compounds. According to Balandin the best catalytic activity for hydrogenation of the benzene ring is shown by substances having a hexagonal or plane-centered cubic structure. Theoretically a platinum catalyst should hydrogenate as well as dehydrogenate. In the hydrogenation of benzene, Packendorff and Leder-Packendorff<sup>87</sup> succeeded in proving that typical dehydrogenation catalysts markedly dehydrogenate at as low a temperature as 170–180°, and that, on the contrary, hydrogenation catalysts at 310° convert benzene into about 30 per cent cyclohexane. The activity of a catalyst is smaller the higher the temperature that has been used in its preparation, and therefore the ability of a catalyst to dehydrogenate may be explained by the fact that its activity is less than that of a hydrogenation catalyst.

Horiuti, Ogden and Polanyi<sup>31</sup> found that, in contrast to the very insignificant hydrogenation of benzene through Pt and Ni at ordinary temperature, a very active exchange of H atoms between gaseous H<sub>2</sub> containing the heavy isotope (in a marked concentration of 1.14 to 20.9 per cent) and the benzene takes place, whereby the heavy hydrogen isotope in the gaseous phase is replaced by the light one from the benzene. The postulated mechanism of hydrogenation is as follows: (1) the benzene molecule splits at the surface of the catalyst, or (2) an adsorbed H atom enters into the adsorbed C<sub>6</sub>H<sub>6</sub>, while another H atom separates. In the second case the separation of the H atom from the benzene molecule may occur either simultaneously with the entrance of the new hydrogen atom or after a certain time has elapsed.

In various catalytic hydrogenations, substances (fatty acids) hydrogenated in the presence of a catalyst, even in the absence of hydrogen in the close vicinity, undergo an intramolecular rearrangement such as a displacement in the position of the double bond. On the other hand, the specificity of many hydrogenation processes, for example the formation of *cis*- and *trans*-isomers from the same product, depending on the kind of catalyst, cannot be explained by simple activation of hydrogen. The fact that certain types of catalysts are suitable only for hydrogenation of definite compounds indicates an additional direct influence of the catalyst upon the second reaction component. Investigations of the mechanism of hydrogenation over solid catalysts seem to indicate that substances to be hydrogenated are deformed in a manner analogous to that of hydrogen.<sup>30</sup> On the assumption that the activity of a hydrogenation catalyst transferring hydrogen, and the reduction potential of a reduction medium are identical concepts, insofar as both determine the reaction velocity of the hydrogen addition process, Ott<sup>86</sup> considered the course of the addition processes in a stereochemical sense as being subjected to the energetic regularity expressed by Ostwald's "Step-rule."<sup>84, 85</sup> In the case of velocities not directly measurable, Ott substitutes for the additional processes the reduction potentials of the used reduction medium. Considering the electro-

motive tension series in the case of the noble metals under the action of electrolytes with smaller reduction potential in hydrogenation, hydrogen is added to the acetylene bond with the formation of only stable ethylene compounds (following the rule of *trans* forms). Starting with a definite point in the electromotive tension series, a mixture of *cis* and *trans* forms originates; and, in the case of the less noble metals, only labile forms of ethylene compounds will be formed (following the rule of *cis* form). Further increase in the reduction potential would cause the velocities of the addition process to reach the point at which ethylene compounds no longer appear as reaction products. In their place according to the Le Chatelier principle, an irregular course sets in and effects the formation of 50 per cent ethane, 50 per cent acetylene remaining unchanged.

Laffitte and Grandadam<sup>46</sup> ascertained from many hydrogenation experiments that  $\text{PtO}_2$  is an excellent catalyst for the hydrogenation of  $\text{C}\equiv\text{C}$  and  $\text{C}=\text{O}$  double bonds and is considerably better than platinum black in this regard. As for the other platinum oxide,  $\text{PtO}$ , it was found to be a good catalyst for the hydrogenation of  $\text{C}\equiv\text{C}$  bonds, but with respect to the  $\text{C}=\text{O}$  bond, its catalytic ability for hydrogen adsorption proved to be mediocre. Platinum oxide alone has been prepared by the action of oxygen upon Pt black under a pressure of 8.25 atmospheres and at a temperature of  $430\text{--}450^\circ$ . At higher oxygen pressures a mixture of  $\text{PtO}$  and  $\text{PtO}_2$  originated between  $410\text{--}420^\circ$ , which became more rich in  $\text{PtO}_2$  as the oxygen pressure increased. Pure  $\text{PtO}_2$  is obtained from these mixtures by treating with aqua regia, in which  $\text{PtO}$  only is soluble.

Assuming with Lowry<sup>50, 51</sup> that the increase in the acidity of ketones with increased bromination is due to the  $\text{C}=\text{O}$  bond changing into a semi-polar bond through change in the electronic state, and that  $\text{OH}'$  as a result of the polarity of the  $\text{C}-\text{Br}$  bond is preferentially bound with increasing bromination, Watson, Nathan, and Laurie<sup>55</sup> interpreted in a corresponding manner the hydrogen migration in enol formation catalyzed by acids or bases. In this case, through a temporary bond of the catalyst, the semi-polar form is converted into an enol or a ketone. The reaction velocity depends, therefore, on the reaction between the ketone and the catalyst and on the part converted from the semi-polar into the enol form. The hydrogen migration in halogenated acetones, phenyl acetones and aliphatic acids has been treated on the basis of quantum mechanical concepts.

The method of differentiating the type of bond activated has been extended to bonds in other compounds subjected to a catalytic reaction. The activation of specific bonds  $\text{C}-\text{H}$  and  $\text{C}-\text{C}$  in ethane on the catalytic surface of Ni on kieselguhr by means of deuterium has been studied by Taylor, Morikawa and Benedict.<sup>50, 51</sup> The reactions investigated were: (1)  $\text{C}_2\text{H}_6 + m\text{D}_2 \longrightarrow \text{C}_2\text{H}_x\text{D}_y (x + y = 6)$ , and  $m$  is optional; (2)  $\text{C}_2\text{H}_6 + \text{H}_2 \longrightarrow 2\text{CH}_4$ . The first reaction corresponds to the activation of the  $\text{C}-\text{H}$  bond and the second reaction to the activation of the  $\text{C}-\text{C}$  bond. It is found that on an activated Ni surface the exchange reaction (I) proceeds quantitatively at  $138^\circ$ , and that at this temperature reaction (II) is insignificant. The formation of  $\text{CH}_4$  according to reaction (II) occurs under the same experimental conditions (about  $150^\circ$ ), and is completed at about

200°. For low  $H_2$  concentration, besides reaction (I)  $C_2H_6 + H_2 = 2CH_4$ , other reactions, such as (II)  $2C_2H_6 = C + 3CH_4$  and (III)  $C + 2H_2 = CH_4$ , may take place. If the catalyst is strongly charged with C, reaction (III) instead of (I) prevails. The activation energy of methane formation from  $C_2H_6$  and  $H_2$  on Ni catalyst was found to be 43 Cal. If ethane is heated alone with Ni catalyst at 218°,  $CH_4$  and C are formed according to (II). The results obtained in this investigation seem to indicate that ethane in the presence of an excess of  $H_2$  suffers a dissociation adsorption to methyl radicals, which are quantitatively converted with adsorbed H into  $CH_4$ . In case of a deficiency of  $H_2$  the dissociation adsorption goes further, from  $CH_3$  to  $CH_2$  to CH and C, with simultaneous formation of atomic H, which with neighboring methyl radicals gives  $CH_4$ . The fact that the exchange reaction takes place with formation of deuterioethane in a temperature interval in which the dissociation adsorption is still subordinate to the formation of the methyl radical, shows that the dissociation adsorption of the ethyl radical and H is a process with a smaller activation energy than adsorption with the formation of the methyl radical. The activation energy for the dissociation adsorption of ethane with formation of the methyl radical was found to be about 19 Cal., while that for the dissociation adsorption with formation of the ethyl radical and H was about 15 Cal.

It has been recognized that in a compound containing many double bonds, which are not conjugated one to another, the bonds may ordinarily be hydrogenated in sequence. While one of the two is almost completely hydrogenated the other is practically unaffected. On the contrary if the double bonds are conjugated one to another by discontinuing the experiment only completely hydrogenated and unhydrogenated compounds are found side by side, there being no partially hydrogenated intermediate products. Thus the system of conjugated double bonds behaves differently in catalytic hydrogenation than in hydrogenations in which, by the origin of a new intermediate double bond, both initial double bonds disappear.

Ginsberg,<sup>24</sup> studying hydrogenation catalysis, proposed classifying compounds to be hydrogenated with respect to their "hydrogen number." The latter represents the cc. of hydrogen adsorbed by one gram of substance at 0° and 760 mm. minus the amount adsorbed by the catalyst. Using catalysts such as Pd—Ni and Pd—Fe, the amounts of hydrogen adsorbed by a catalyst (0.1 g.  $PdCl_2$ , 2NaCl and 1 g. Ni) were determined at different intervals of time.

Ablesowa and Roginsky<sup>1, 2</sup> measure the activity of Ni with respect to its hydrogenation capacity as a function of the hydrogen gas content in the layer. The curve obtained thereby indicates a maximum with a very steep drop to both sides. The maximum corresponds to the ratio 1  $H_2$ :100 Ni. In hydrogenation through adsorbed hydrogen atoms on fresh Cu and Ni layers, both hydrogen and ethylene are markedly adsorbed. However, if such a layer is heated it loses the ability to retain these gases. Atomic H is adsorbed also by previously heated layers at the temperature of liquid air and on such layers ethylene also is deposited. Yet at room temperature both gases remain adsorbed and are able to form an intermediate compound. By a further increase in temperature, hydrogenation leads to ethane formation.

Zelinsky, Kasansky and Plates,<sup>33</sup> studying the hydrogenation of cyclopentane and its simplest homologs, observed certain peculiarities indicating that the splitting of the cyclopentane ring occurs at the surface of the catalyst only in the presence of an excess of hydrogen. Hydrogenation of homologs of cyclopentane, such as methyl and ethyl cyclopentane, in the presence of platinized charcoal at 305–315° leads to a decomposition into iso-forms rather than isomers. Thus an example of destructive hydrogenation under atmospheric pressure and moderate temperature takes place.

The mechanism of catalytic hydrogenation of organic fluorine compounds such as cyclohexyl fluoride has been interpreted<sup>78</sup> in the sense that fluorine adhering to the aromatic nucleus is exchanged for hydrogen during hydrogenation, but the aliphatically bound F is not exchanged. The splitting off of F may of course either precede the ring hydrogenation or follow it. In the latter case cyclohexyl fluoride should be readily reduced catalytically to cyclohexane, but this is not the case. From the fact that 8 g. of  $C_6H_{11}F$  over 0.5 g. of Pt adsorb in 6 hrs. only  $1.01 \times 10^{-3}$  g. mol of H and  $1.06 \times 10^{-3}$  g. mol of HF, while 9.9 g. of  $C_6H_5F$  under equal conditions adsorbs in 95 minutes  $4.9 \times 10^{-2}$  g. mol of H and  $1.18 \times 10^{-2}$  g. mol of HF, it has been concluded that the splitting off of HF occurs before, not after, ring hydrogenation. The electronic theory has been used for the explanation.

Foresti<sup>17</sup> attempted to correlate the structure of the electrical double-layer of platinized Pt with the hydrogenation velocity of benzene in a liquid medium such as 1.0N HCl, 2 and 3N KCl solution with added HCl. The dependence of the hydrogenation velocity of benzene on the pH has been studied. A pronounced maximum of hydrogenation velocity at pH = 1.0 to 2.0 has been observed by the transition from an alkali to an acid medium. In the reverse procedure the hydrogenation velocity has been greatly decreased in strong acid media on the addition of small amounts of alkali. From the fact that, with increase of pH not only the amount of ions electrostatically adsorbed on the electrical double-layer is increased, but simultaneously an exchange of hydrogen ions for metallic cations is stimulated, a kind of gradual, reversible poisoning may be postulated. It has been thought also that the double layer possesses unequal dielectric values and that the zones of greater dielectric values correspond to the most active parts of the catalyst—platinized Pt—H<sub>2</sub> electrode. The maximum of the reaction velocity is found at the zero point of the electrode charge, which coincides with the potential determined by Frumkin.<sup>20, 21</sup>

Furthermore, Foresti and Chiummo,<sup>18</sup> investigating the hydrogenation of ketones with Pt black poisoned with thiophene and with Pt-plated Ni, obtained equal results for these catalysts. Only the hydrogenation of the keto- group took place, and this has been considered as proof of the fact that the hydrogenation velocity of organic substances is influenced by the pH of the medium in two different and opposite ways. First, activation follows by a drop in pH at the catalytic surface; secondly, activation in the opposite direction may occur if, through the chemical properties of the substance to be hydrogenated, an activation in an alkali medium is possible. The first process is observed likewise in the case of the Raney Ni catalyst. However, Ni in the pH region where it is catalytically active may



act as a hydrogen electrode. But there is no doubt as to the influence of pH on the catalytic activity of Pt black.

In an attempt to interpret hydrogenation catalysis Dolliver, Gresham, Kistiakowsky and Vaughan<sup>13, 14</sup> studied the relationship between the structure and the hydrogenation heat of unsaturated hydrocarbons. The heats of hydrogenation of organic compounds were determined calorimetrically at temperatures from 82–109°, and were then recalculated to 82° in Cal./Mol.

Table 1. Heats of Hydrogenation of Organic Compounds.

Substance	Number Hydrogen Added	Heats of Hydrogenation (Cal./Mol)
Ethyl benzene.	+3H <sub>2</sub>	-48920
<i>o</i> -Xylene.	+3H <sub>2</sub>	-47250
Mesitylene.	+3H <sub>2</sub>	-47620
Styrol.	+4H <sub>2</sub>	-77480
Hydrindol.	+3H <sub>2</sub>	-45800
Indol.	+4H <sub>2</sub>	-66910
Cyclopentene.	+ H <sub>2</sub>	-26915
<i>a</i> -Phellandrene.	+2H <sub>2</sub>	-53410
<i>a</i> -Terpinene.	+2H <sub>2</sub>	-50705
Limonene.	+2H <sub>2</sub>	-54110
Isopropylethylene.	+ H <sub>2</sub>	-30336
<i>neo</i> -Amylethylene.	+ H <sub>2</sub>	-29532
<i>tert</i> -Butylethylene.	+ H <sub>2</sub>	-30341
2,4,4-Trimethylpentane-1.	+ H <sub>2</sub>	-27236
2,4,4-Trimethylpentene-2.	+ H <sub>2</sub>	-28392
Pentadiene-1,3.	+2H <sub>2</sub>	-54112
2,3-Dimethylbutadiene-1,3.	+2H <sub>2</sub>	-53872

The assumption previously made, namely, that substitution in chain branching generally leads to a stronger decrease in hydrogenation heat, has been revised. For example, it has been stated that the introduction of chain branching in the proximity of a double bond cannot be expressed by simple rules with respect to hydrogenation heats. The hydrogenation heats of 5-membered ring systems were found to be lower than those of comparable 6-membered compounds. As an explanation of this difference it was suggested that higher tensions exist in the 5-membered ring, which bring about a condition such that by hydrogenation a part of the available energy is set free, but not as heat. The results in the case of aromatic compounds also differ from those obtained for aliphatic. Hydrogenation heats of some unsaturated esters such as ethyl-, propyl-, butyl-, isobutyl-, secondary propyl and butyl esters of crotonic acid, propylidene acetic acid,  $\beta$ -ethylidenepropionic acid and allyl acetic acid were determined by considering the combustion heats of the corresponding saturated compounds.<sup>63</sup> When the C=C bond is in the  $\gamma$ ,  $\delta$  position to the carboxyl group, the measured heat of hydrogenation is in agreement with the values observed by hydrogenation of ordinary aliphatic double bonds. From this fact it has been deduced that the C=C double bond and the carbonyl bond do not influence one another in the  $\gamma$ ,  $\delta$ -unsaturated esters. However, this conclusion contradicts the conceptions of Hiltner<sup>29</sup> who calculated the affinity for the reduction potential of crotonic acid and butyric acid. But Hiltner did not prove that the measured reduction systems are reversible, and there-

fore there is no evidence that the measured potentials may be considered as the true reduction potential.

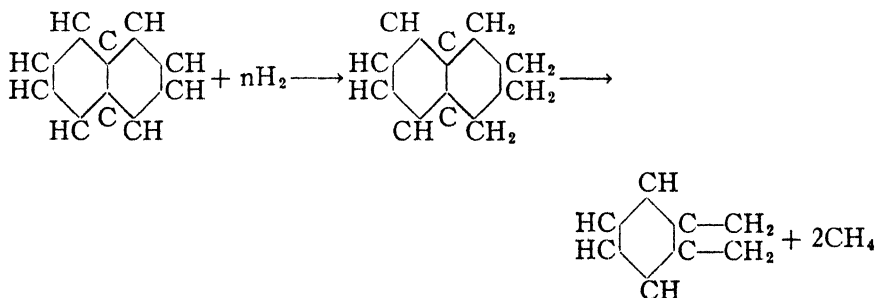
A. and L. Farkas,<sup>15</sup> discussing hydrogenation reactions of unsaturated compounds, pointed out two different independent mechanisms: (1) In catalytic hydrogenation both hydrogen atoms of a molecule accumulate simultaneously at the unsaturated bond, while in the case of hydrogenation with nascent hydrogen two independent free atoms are added, one after another. From this point of view, the catalytic hydrogenation of ethylene derivatives with nascent hydrogen would give *meso* derivatives, while molecular hydrogen would give either the *meso* or the optically active form, depending on whether the *trans* or the *cis* form was being hydrogenated. The thermodynamically more stable compounds are mostly the *trans*-ethylene derivatives or the *meso* compounds. Exceptions may exist, which are explained by catalytic rearrangement of the primary, originally unstable product into more stable forms. Experiments on the catalytic exchange of hydrogen atoms between gaseous hydrogen and organic compounds have shown that exchange reactions occur only in di-substituted ethylene derivatives or in compounds that contain a carbonyl group. Hydrogenation with nascent hydrogen shows a great similarity to halogenation of unsaturated compounds in the sense of formation of stereoisomers.

Farkas<sup>15a</sup> investigated the catalytic hydrogenation with parahydrogen and found that the mechanism involves a simultaneous addition of two hydrogen atoms to the multiple bond. By catalytic exchange action between hydrogen and hydrocarbons, a hydrogenation and an exchange of hydrogen atoms between the hydrocarbon and the molecular hydrogen may take place. The catalytic exchange proceeds with a partial splitting of the hydrocarbon into hydrogen atoms and hydrocarbon radicals on the surface of the catalyst. Thus the catalytic activation of hydrogen molecules occurs with formation of atoms at the surface of the catalyst. The dissociation velocity may be measured by means of the *ortho-para* conversion of hydrogen or deuterium, or by the reaction:  $\text{H}_2 + \text{D}_2 = 2\text{HD}$ . From this indicator reaction conclusions may be drawn regarding the composition of the adsorption layer on the catalyst. The concentration of the reaction partner in the adsorption layer is the deciding factor for the velocity of the exchange action of hydrogen with the hydrocarbon. The mechanism proposed is in agreement with results given in the literature for the formation of stereoisomers in hydrogenation reactions. In addition to exchange reactions with saturated and unsaturated hydrocarbons, the catalytic *cis-trans* isomerization and racemization of stereoisomers, the migration of double bonds, the disproportionation of cyclohexanes and related compounds, as well as some polymerization reactions, have been interpreted by Farkas in the light of the mechanism proposed. This investigator, in a further study of the catalytic exchange of hydrogen atoms between molecular deuterium and *n*-hexane, as well as cyclohexane, over a platinized platinum foil, states that the reaction:  $\text{C}_6\text{H}_{12} \rightleftharpoons \text{C}_6\text{H}_6 + 3\text{H}_2$  is not significant for the kinetics of the hydrogen exchange as shown by special measurements of the dehydrogenation velocity of cyclohexane; rather it may be

assumed that in both exchange reactions a dissociation of the hydrocarbons in hydrogen atoms and radicals precedes the adsorption of deuterium.<sup>16b</sup>

The recognized types of hydrogenation catalysis are: (1) Normal hydrogenation, in which molecular hydrogen combines with a molecule of the organic compound to be hydrogenated, or in which atoms of oxygen are replaced by hydrogen, forming saturated hydrocarbons. Ordinary double bonds are hydrogenated regardless of position by Zn, Cu, Mn, Sn. (2) Selective hydrogenation in which the choice of the catalyst definitely determines the product yielded. For example, hydrogenation of allyl benzene over CuO under pressure gives propyl benzene as the only product, whereas hydrogenation of allyl benzene over Ni or Co oxides results in propyl cyclohexane. Selective hydrogenation is particularly observed in the case of hydrogenation of terpenes and oxygen-containing terpenes (eugenol, anethol, etc.). CO is hydrogenated by metals to CH<sub>4</sub>, but with ZnO may be converted into methanol. (3) Intermolecular hydrogenation is understood in the sense that one molecule of a hydrocarbon loses its hydrogen atoms, and that this atomic hydrogen then combines with a molecule of another hydrocarbon, hydrogenated under given conditions. Ipatieff and Pines, when studying polymerization of ethylene under pressure over H<sub>3</sub>PO<sub>4</sub> catalyst, obtained evidence for the fact that intermolecular hydrogenation may take place without the introduction of H<sub>2</sub>. (4) Destructive hydrogenation takes place when the organic substance under thermal decomposition forms fragments or radicals with which hydrogen combines, forming saturated molecules of a smaller molecular weight: C<sub>10</sub>H<sub>22</sub> + H<sub>2</sub> → C<sub>6</sub>H<sub>14</sub> + C<sub>4</sub>H<sub>10</sub>. Excess of H<sub>2</sub> and pressure serve to prevent carbon formation.

The destructive hydrogenation of unsaturated organic compounds, together with aromatic substances such as naphthalene, fluorene and phenanthrene, was considered by Ipatieff to consist of two phases: (a) hydrogen attaches itself to the aromatic nucleus, and (b) the resulting incompletely hydrogenated hydrocarbon decomposes into a substituted mononuclear aromatic hydrocarbon according to the scheme:



at a temperature of 425–450°, 70–80 atmospheres' initial pressure of H<sub>2</sub>.

Adkins<sup>8</sup> differentiates the action of H<sub>2</sub> with respect to organic compounds, depending upon whether hydrogen is added to a multiple linkage, and this is

termed hydrogenation; or cleavage of a molecule takes place, which corresponds to hydrogenolysis. (5) Finally, the hydrogenation and polymerization process may be combined.

### Industrial Hydrogenation Processes

Catalytic hydrogenation in many instances has found application on an industrial scale. Hydrogenation or solidification of liquid fatty oils known since Debus (1863) and De Wilde (1874) over Pt catalyst and industrially applied first by Sabatier and Senderens (1897) and Normann (1902) over Ni catalyst, constitutes a striking example of an industrial hydrogenation process. The output of hydrogenated fats greatly exceeds that of other hydrogenation products because of the wide scope of its application (in soaps, candles, and edible products) and the small amount of hydrogen necessary for the process. The production of hydroaromatic derivatives from phenol, cresols, and naphthalene, as well as menthol from thymol, is well known. Hydrogenation finds major adaptations in the petroleum industry for it serves: (1) to improve low-grade lubricating distillates; (2) to convert paraffinic or aromatic gas oils into stable gasolines; (3) to produce Diesel fuels of high Diesel index, low sulfur content, and good color from low-grade distillates; (4) to convert heavy asphaltic crude oils and refinery residues, without appreciable coke formation, into gasoline and a distillate free from asphalt and of low sulfur content; (5) to desulfurize badly gumming and sulfur-rich naphthas; (6) to produce kerosenes of superior burning characteristics, as well as naphthas of high solvent power to be used as lacquer diluents, and (7) to produce aviation fuels of high anti-knock quality and with high flash point.

Hydrogenation of coal and its distillation products, known since the investigations of Bergius in 1914 and industrially applied in 1925, is a catalytic process of major significance in certain countries. Hydrogenation of coal is cracking superimposed on the hydrogenation process. When, at the moment the hydrocarbons split up, hydrogen becomes attached to the fragments, compounds rich in hydrogen and of low molecular weight are formed and coke-formation is eliminated. In hydrogenation of coal two types of catalysts find application: various Sn compounds and Mo sulfide. While the latter is used for hydrogenation in the liquid or vapor phase, Sn compounds are applied for the hydrogenation of coal as such. The relative effectiveness of the catalyst is a function of its age and the general characteristics of the coal treated. It is stated that with some coals Mo compounds are more active than those of tin in the production of liquid hydrocarbons.

Coal may be hydrogenated in the form of a powder or suspended in a suitable high-boiling oil. Usually a paste consisting of coal and an oil vehicle containing a small percentage of a tin compound is hydrogenated at about 450° under high pressure; the liquid products obtained are fractionated, and the heavy oil rehydrogenated in the presence of Mo compounds. Formation of considerable methane is a sign of too extensive gasification, while the formation of heavy oils and coke indicates too great a

dissociation. Formation of phenols not desirable in this conversion is favored by the use of catalysts displaying a tendency to change the stages of valence. Catalytic substances which work for some time contain the metal in various stages of valence. The general effect of increase in temperature is that both hydrogenation and cracking processes are accelerated. However, the increase of temperature reduces the degree of hydrogenation possible and therefore an upper limit has to be recognized. The effect of temperature on hydrogenation of coal has been graphically

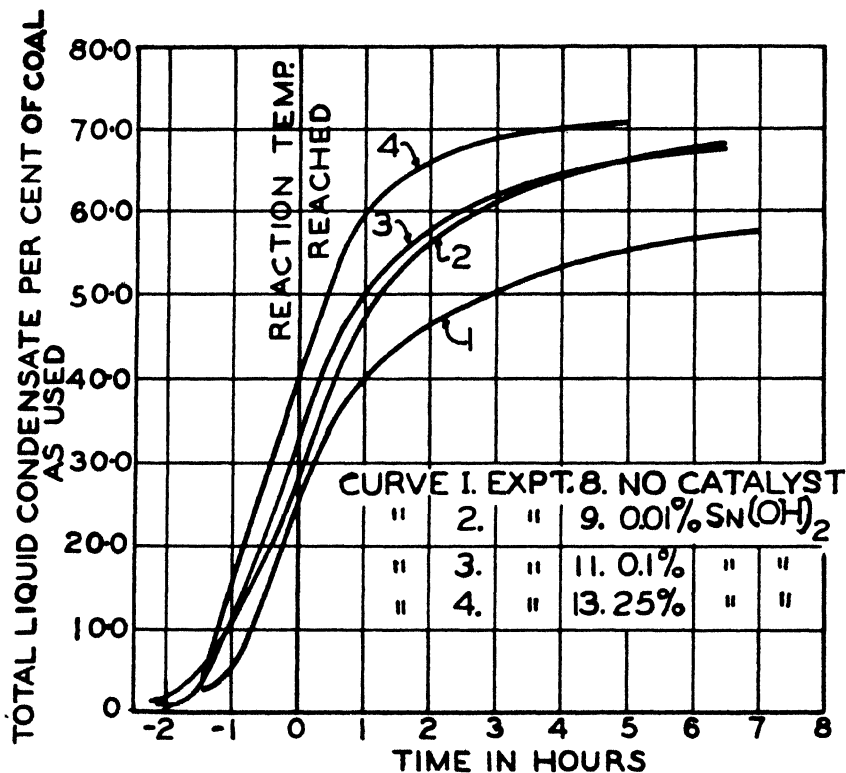


FIGURE 4.—Rate of Production of Liquid Products from Coal in the Presence of Vehicle.

expressed by Gordon.<sup>26</sup> He found that as the temperature rises the residue of carbonaceous matter decreases, the total yield of oil decreases, more gas and little more water are formed, and the nature of the oil is changed. Too high a temperature yields more gas without affecting the amount of middle oil. Too low a temperature has the opposite effect. Horton, King and Williams<sup>22</sup> have heated coal to a reaction temperature in a stream of  $\text{H}_2$  and measured the rate of production of oil. The comparative rates are illustrated in Figure 4.

Increase in time of contact in hydrogenation of coal has the same effect as an increase of temperature. It has been found that at  $440^\circ$  an increase

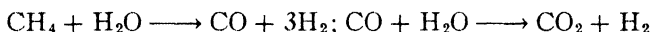
in the reaction time from 2 to 4 hours is equivalent to a rise in temperature of 20°.

King<sup>41</sup> registers the effect of pressure on the hydrogenation of Beam-show (Yorkshire) coal.

Table 2. Effect of Pressure on the Hydrogenation of Yorkshire Coal.

—Pressure (atm.)—		Products		
Initial	Maximum	Solids	Water	Oil
80	203	41.2		37.2
100	245	26.1	6.1	50.2
120	283	21.6	6.4	56.7

The amount of hydrogen used in the hydrogenation of coal is about 50,000 cu. ft. per ton of coal treated. This hydrogen is usually supplied by interaction of gaseous hydrocarbons with steam:



Provision is made for removing sulfur prior to treatment with hydrogen. Likewise hydrogen may be produced either directly from coke and steam or by separating it from coke oven or other gases. The process may be self-contained with respect to hydrogen, if 15 per cent of the carbon content of the coal treated is converted into gaseous hydrocarbons.

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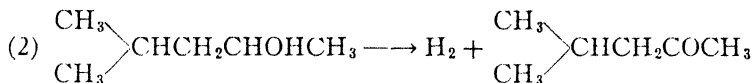
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## PART IV

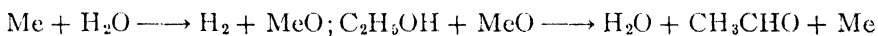
### Catalytic Dehydrogenation

Dehydrogenation reactions may be viewed as decomposition processes in which hydrogen is set free. Often, however, dehydrogenation with specific catalysts is more advantageous than simple pyrolysis. Thus, for example, to obtain olefins, catalytic dehydrogenation may give better results than simple pyrolysis of paraffins. In the latter case the yield is smaller and the hydrogen is rendered impure by such gases as methane and ethane. A pure catalytic splitting may be represented by the dehydrogenation of ethane to ethylene:  $\text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_4 + \text{H}_2$ . A suitable catalyst may stop the splitting at the stage of ethylene formation. As examples of dehydrogenation reactions embodying simultaneously a thermal decomposition may be cited the decomposition of primary alcohols passed over iron filings at 460-480°, forming aldehyde and hydrogen according to the equation:  $\text{RCH}_2\text{OH} \longrightarrow \text{H}_2 + \text{RCHO}$ . Likewise, vapors of a secondary alcohol decompose to form a ketone and hydrogen, expressed as:  $\text{RCHOHR}_1 \longrightarrow$

$\text{H}_2 + \text{RCOR}_1$ . Isopropyl alcohol and methyl isobutyl carbinol were found to decompose in an iron tube at  $600^\circ$  according to schemes:



Ipatieff,<sup>9</sup> discussing catalytic dehydrogenation of alcohols, drew a comparison between the decomposition of an alcohol and water in the presence of a metal (Fe). He stated that the difference lies in the fact that the oxygen of alcohol remains joined to the carbon atom and that the catalyst iron remains unchanged, whereas in the decomposition of water its oxygen does not remain intact but combines with the metal, forming an oxide; therefore the latter reaction is a non-catalytic. This is illustrated by the two equations:



Nickel has been found inferior to iron as a dehydrogenation catalyst.<sup>10, 11</sup> Carbon formed from alcohol at high temperature in the presence of pumice has been found to be a good catalyst for its dehydrogenation. Sabatier and Maihle,<sup>22</sup> tabulating the action of a large number of metal oxides, classified them into those exclusively suited for dehydrogenation of alcohols, such as Mn and Sn oxides; those possessing only a dehydrating action, like Th and Al oxides; and finally those causing both dehydration and dehydrogenation, such as for example, uranium oxide.

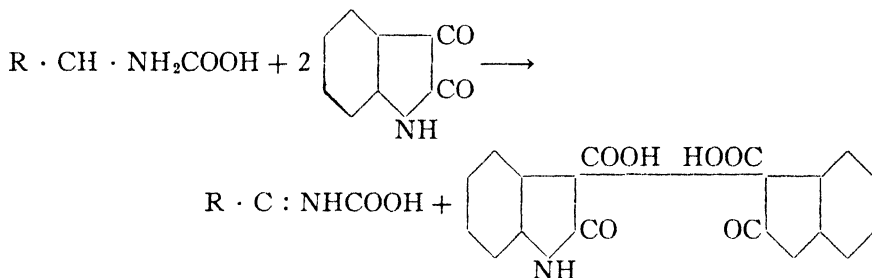
Constable,<sup>4</sup> studying the dehydrogenation of primary alcohols over copper as catalyst, assumed that alcohol molecules form a monomolecular layer on the surface of the catalyst, the arrangement of the molecules being such that the hydroxyl groups are directed toward the copper atoms, while the hydrocarbon chain is perpendicular to the copper surface. The action of the catalyst is considered to be a result of adsorption forces; the distance between the hydrogen and the oxygen atoms of the hydroxyl group is increased, and the oscillation energy required for splitting off neutral hydrogen atoms is decreased. The activity of the copper surface is considered to be limited to single reaction centers. A mathematical expression of the dehydrogenation velocity has been deduced from the point of view of static mechanics, whereby it was found to depend neither on the velocity at which the substance to be dehydrogenated is passed through the catalyst nor upon the pressure.<sup>19</sup>

Adkins and Lazier<sup>1, 2</sup> found the relationship between dehydration and dehydrogenation to be independent of the structure of the alcohol being treated, but dependent on the nature of the catalyst. It has been stated by Taylor and Levin<sup>24</sup> that a purely dehydration catalyst accelerates chiefly the H—OH recombination, while a typical dehydrogenation catalyst affects the H—H recombination. Should the latter assumption hold true, as asserted by Lavin and Jackson,<sup>15</sup> then a dehydrogenation catalyst promoting the H—H recombination would give up OH—H in the



reaction, and the OH radicals may be separated from the H atoms when the latter are permitted to recombine on a dehydrogenation catalyst.

The mechanism of dehydrogenation of amino-acids catalyzed by organic catalysts was described by Langenbeck<sup>13, 14</sup> as follows: (1) Isatine is hydrogenated by the hydrogen of the CH—NH<sub>2</sub> group of alanine to form "isatide," a pinacone-like compound.



The amino-acid originating in the manner described is then hydrolyzed with decarboxylation to the aldehyde and ammonia, according to the following equation:  $\text{R} \cdot \text{C} : \text{NH} \cdot \text{COOH} + \text{H}_2\text{O} \longrightarrow \text{R} \cdot \text{CHO} + \text{NH}_3 + \text{CO}_2$ . For the dehydrogenation of one molecule of amino-acid two isatine molecules are required in the absence of an oxidizing agent, while in the presence of air, oxygen or even methylene blue as a hydrogen acceptor, the isatide is regenerated to isatine with formation of water, hydrogen peroxide or leuco-compounds of methylene blue. Thereby hydrogen taken up from the amino-acid is given off and the function of the catalyst as a hydrogen transferer is renewed. This reaction mechanism has been considered by Langenbeck as an indication that the catalyst may function in the dehydrogenation of a considerable number of molecules of the original  $\alpha$ -amino acid.

In order to explain the selective dehydrogenation in the case of hexahydroaromatics Balandin<sup>3</sup> proposed that catalytic dehydrogenation occurs when a group of surface atoms appropriately spaced and of the necessary activity absorb the reactant in a definitely oriented position. This interpretation was called the "multiplet hypothesis" because of the simultaneous action of several surface atoms. A compound having a hexagonal structure, for example, cyclohexane, is adsorbed upon a network of atoms which form a triangle, in such a manner that each atom of the catalyst (vertex of the triangle) lies midway between two carbon atoms of the ring; dehydrogenation occurs when half of the hydrogen atoms from adjacent carbon atoms are drawn close together, so as to form a hydrogen molecule at the nearest surface catalyst atom. On the basis of this hypothesis Balandin interpreted the following experimental findings: (1) cyclopentane and cycloheptane, being 5 and 7-membered rings respectively, are not dehydrogenated by metal catalysts; (2) cyclohexene and cyclohexadiene are not obtained as products of partial catalytic dehydrogenation of cyclohexane; (3) di-substituted cyclohexane is not dehydrogenated by metal catalysts when the substituted groups are attached to the same carbon atom.

Dehydrogenation has been interpreted also on the basis of the free radical mechanism and limited to the types of reactions representing the primary non-catalytic decomposition.<sup>20</sup> The first step in dissociation of methane was assumed to be the scission of a single C—H bond, forming a methyl radical:  $\text{CH}_4 \rightleftharpoons \text{CH}_3 + \text{H}$  or  $\text{CH}_4 \longrightarrow \text{CH}_2 + \text{H}_2$ . The experimentally determined heat of activation has been considered to favor the latter reaction.

Table 1. (Rice).

Reaction	Energy of Activation (Cal.)
$\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$	-100,000 (-125,000)
$\text{CH}_4 \rightarrow \text{CH}_2 + \text{H}_2$	-47,000 <sup>22</sup>
$2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2^{12}$	—
$\text{CH}_3 \rightarrow \text{CH}_2 + \text{H}$	-100,000
$\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3$	-79,500
$\text{CH}_3\text{CH}_3 \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}$	49,000
$\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$	> 20,000
$\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{H}_2 + \text{C}_2\text{H}_5$	17,000
$\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$	23,000
$\text{C}_2\text{H}_5 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}$	25,000
$\text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5$	20,000

It has been assumed that the  $\text{CH}=\text{CH}$  radical participates in dehydrogenation reactions on collision with acetylene molecules, as shown in the following equation:



Frey and Smith<sup>7</sup> and Marek and McCluer<sup>18</sup> studying dehydrogenation of paraffin hydrocarbons, suggested from their data that hydrogen separates directly from the hydrocarbon as a molecule, rather than by the free radical mechanism. Rice and Dooley<sup>21</sup> objected to this, pointing out that there is a relation between the structure of the hydrocarbon and the extent of the dehydrogenation process. That this is not the case has been indicated by data obtained by Frey and Hepp.<sup>6</sup> At 600°, propane gave 23.0%  $\text{H}_2$  in the product; *n*-butane gave only 4.5%, and isobutane gave 26.4% (not due to a tertiary hydrogen atom, because 2,3-dimethylbutane gives only 3%  $\text{H}_2$ ).

Referring to members of the paraffin series, it is interesting to note that they were found to dehydrogenate by the action of alpha radiation.<sup>16, 17</sup> At 25° alpha radiation from radon caused the elimination of  $\text{H}_2$  from methane and formation of saturated gaseous hydrocarbons and an unsaturated liquid product of the empirical formula  $\text{C}_n\text{H}_{1.98n}$ . Unsaturated hydrocarbons were not detected among the gaseous reaction products.

Dintzes and Frost<sup>5</sup>, investigating the dehydrogenation of propane, found that it decomposes into hydrogen and propylene as well as into methane and ethylene. The experimental results were not in agreement with the unimolecular law but complied with the equation:

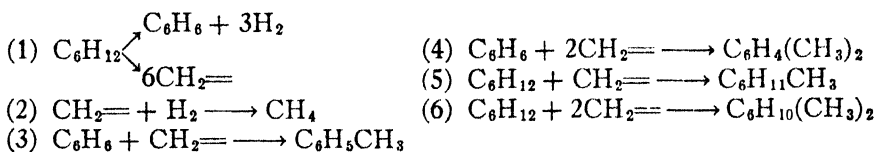
$$K = \frac{1}{t} \left( \ln \frac{1}{1-x} - \beta_x \right)$$

where  $\beta$  is independent of pressure and temperature. Pure propane introduced into the reaction chamber containing decomposed propane decomposed at a slower rate than either pure propane or a mixture of propane and its final decomposition products. The writers considered these facts to be indicative of a chain mechanism and not to coincide with the unimolecular theory.

The most frequent reaction of cycloparaffins and cycloolefins containing six-membered rings is their dehydrogenation to the corresponding aromatics, to the partially hydrogenated aromatics, or to both. In the group of compounds containing six-membered rings, the most probable primary reactions are considered to be those with a C—H scission in the ring, or a C—C or C—H break in the chain of the molecule; less frequently, a C—C break or rupture of the ring occurs. In most cases the dehydrogenation of the ring to the corresponding hydrocarbon has been regarded as a primary action, the secondary action being a function of the thermal reaction of that aromatic in the presence of hydrogen formed by the primary action, and of the unreacted hydrogenated molecules. With respect to cycloparaffins and cycloolefins containing rings of 3, 4, 5, 7 and 8 carbon atoms it is known that they also react in several ways. The most frequent reaction involves a splitting of a single C—C bond to open the ring, forming an olefin, in addition to which other products may be formed from the decomposition of the original open-chain hydrocarbon. On the other hand there are reactions which may involve the C—C and C—H break in the side chains.

Zelinsky<sup>25</sup> found that benzene passed over Pd black in the presence of H<sub>2</sub> at 100–110° gave a good yield of cyclohexane and at 300° almost a quantitative yield of benzene and hydrogen. With Pd at a temperature above 200° dehydrogenation was observed, while below 200° hydrogenation occurred. He believed first that the dehydrogenation takes place by six hydrogen atoms splitting off simultaneously without intermediate formation of di- and tetrahydro-aromatics. A single passage of cyclohexane through a tube at 300° produced 80.5 per cent H<sub>2</sub> with Pd as catalyst and 62.5 per cent H<sub>2</sub> with Pt as catalyst. Zelinsky was of the opinion that the decomposition over Pt or Pd black is a dehydrogenation reaction and not a ring rupture to form methane, as in the case of Ni catalyst.

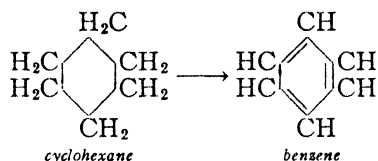
In a more recent work Zelinsky and Shujkin<sup>26</sup> again studied the dehydrogenation of cyclohexane and found that the latter undergoes dehydrogenation to form benzene, which further decomposes to form the free methylene radical when heated in a hydrogen atmosphere at 330–350° in the presence of Ni precipitated on Al(OH)<sub>3</sub>. The mechanism proposed to explain the products obtained is as follows:



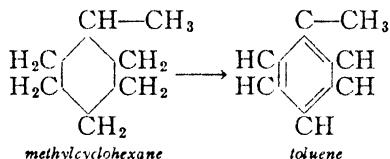
Together with benzene, CH<sub>2</sub>= radicals are formed, which in part are

reduced to methane, while toluene, xylene, methylcyclohexane and dimethylcyclohexane are formed.

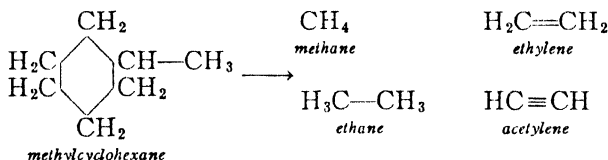
Just as benzene is obtained from cyclohexane by dehydrogenation,



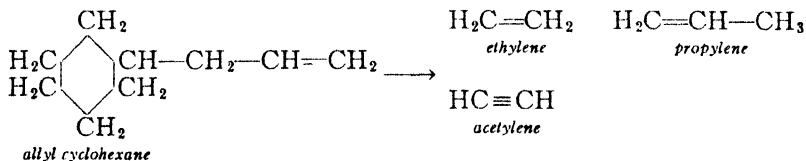
wherein a chain of dehydrogenation steps with intermediate radicals is postulated, so toluene is obtained by dehydrogenation of methylcyclohexane:



In this reaction a change in the side chain, as well as a break at the C—H in the ring is involved. The simple hydrocarbon, methylcyclohexane, severs the C—C bond between side chain and ring to form a methyl radical, which subsequently hydrogenates to methane, and the remaining radical undergoes further hydrogenation to form ethylene and acetylene.

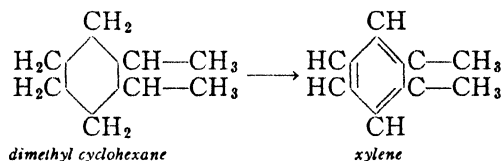


Likewise allyl cyclohexane breaks at the C—C bond between the side chain and ring, forming a propenyl radical, which may hydrogenate to propylene or break down to vinyl, which either hydrogenates to ethylene or dehydrogenates to acetylene.

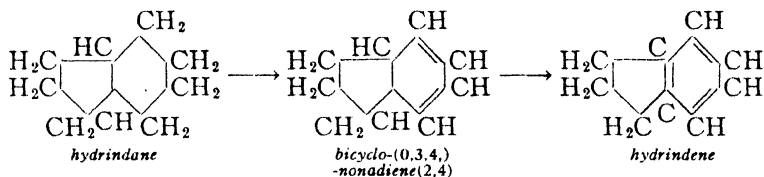


Thus alkylated six-membered ring cycloparaffins and cycloolefins yield not only the corresponding aromatics, but also end-products resulting from either C—C or C—H breaks in the side chain alone with no change in the ring structure. The intermediary radicals formed may also include free valences from the splitting of one bond in the C—C linkage of the side chain. The alkyl substituents on the product are the same as those on the starting hydrocarbon and the only change effected is a break at the C—H

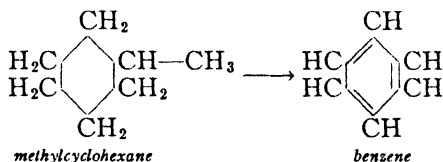
bond in the ring. The dehydrogenation of dimethyl cyclohexane to xylene may be considered as an example.



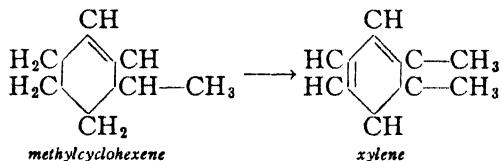
Another hydrocarbon containing a six-membered ring which yields dehydrogenation products by severance of the C—H bonds in the ring is hydrindane.



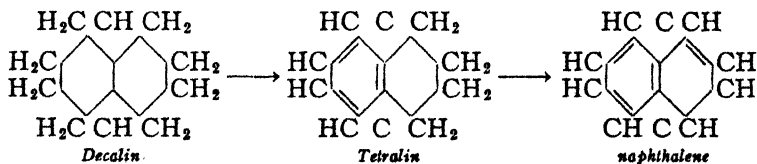
Combination of two mechanisms of dehydrogenation is observed in cases in which the C—C linkages are broken in the side chain, while simultaneously the C—H bonds of ring members are being broken. The dehydrogenation of methylcyclohexane to benzene may serve as an example.



Also in the case of methylcyclohexene severed methyl groups may attach themselves to the dehydrogenated ring structure to yield xylene.



In the case of various naphthenes derived from naphthalene by hydrogenation, dehydrogenation to the corresponding aromatics is also a predominant reaction. It has been ascertained not only that Decalin is dehydrogenated to naphthalene according to the following scheme:



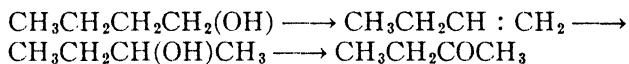
but that it also forms the partially hydrogenated Tetralin, and the latter as well as decahydronaphthalene yields the basic aromatic naphthalene. In each of these cases the primary break is at the C—H bond in the hydrogenated rings.

The most important industrial use of dehydrogenation processes is the production of formaldehyde, acetaldehyde, butyric aldehyde and methyl ethyl ketone from alcohols. The aqueous solution of formaldehyde is called Formalin and usually contains 38–40 per cent of formaldehyde and 10–20 per cent of methyl alcohol. However the I. G. Farbenindustrie A.-G.<sup>8</sup> claimed the production of 60-per cent Formalin solution using anhydrous methyl alcohol. Ordinary 40-per cent Formalin is manufactured on a large scale and used as an antiseptic and disinfectant. It is used in the preparation of hexamethylenetetramine (hexamine) which is a condensation product of 6 molecules of formaldehyde and 4 molecules of ammonia.

Formaldehyde is used in the manufacture of synthetic resins by condensation with phenols (Bakelite) or with urea. Formaldehyde is the ingredient of certain dyestuffs (of the amidine series) and of other synthetic organic compounds. Preparation of acetaldehyde by combining dehydrogenation and oxidation is a process competing industrially with aldehyde produced by hydration of acetylene.

Although propyl and isopropyl alcohol are readily dehydrogenated to propionic aldehyde and acetone, these reactions do not possess industrial significance.

Methylethyl ketone is manufactured by dehydrogenating methylethyl carbinol or it may be obtained from the conversion of normal butyl alcohol. The process occurs as follows:



Dehydrogenation of olefins, which are initial materials for polymerization to gasoline, lubricating oils, drying oils, resins, rubber and other chemical derivatives, is recognized as an established industrial process.

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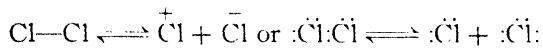
## PART V

## Catalytic Halogenation

In general, halogen substitution can be either photochemical and non-ionic or polar and influenced by ionic catalysis. The photochemical reaction  $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$  is the same type of reaction as  $\text{CH}_4 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{—Cl} + \text{HCl}$ , in which a hydrogen of an aliphatic compound is replaced by a halogen. Halogen substitution in ketones proceeds through an intermediate enolic form; in an aromatic nucleus it proceeds at low temperatures and in the absence of light, but under ionic conditions in the presence of polarizing catalysts, such as iodine, chlorine, ferric salts, or pyridine. Although aromatic compounds like the paraffins are very stable, they undergo instantaneous halogenation because they react readily in substitution processes. The mechanism of halogen substitution, for instance the chlorination of toluene, provides two possibilities:

(1) Substitution in the side-chain:  $\text{C}_6\text{H}_5\text{—CH}_3 + \text{Cl}_2 \longrightarrow \text{C}_6\text{H}_5\text{—CH}_2\text{—Cl} + \text{HCl}$ ; this is a case under non-ionic conditions in the vapor phase and exposed to light.

(2) Nuclear substitution:  $\text{C}_6\text{H}_5\text{—CH}_3 + \text{Cl}_2 \longrightarrow \text{ClC}_6\text{H}_4\text{—CH}_3 + \text{HCl}$  in darkness at a low temperature, but catalyzed by polar substances. The reaction of chlorination or bromination of ethylene proceeds preferentially under unsymmetrical polar conditions. According to the theory of the amphoteric character of halogens advocated by Noyes,<sup>26</sup> unsymmetrical fission of a halogen molecule results in rupture of the covalent bond to form a pair of oppositely charged ions:



The action of halogens with water:  $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HClO}$  is expressed as depending on an interchange of ions as follows:

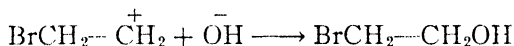


It has been postulated by Norrish<sup>24, 25</sup> that addition of halogen proceeds more readily by a polar than by a non-polar mechanism. Halogenation of ethylene in polar solvents or in contact with polar substances as catalysts has been assumed to be a two-stage ionic process with  $(\text{C}_2\text{H}_4\text{Br})^+\text{Br}^-$  as an intermediate compound. Norrish's experiments seemed to indicate that a polar catalyst promotes the interaction of ethylene and bromine and that the halogenation process is ionic in character. It has been thought that addition of halogens is a non-polar action only under the influence of light and that, if this holds true, the difference between the two types could be shown by the interaction of benzene with chlorine, since an addition compound of the type  $\text{C}_6\text{H}_6\text{Cl}_6$  would be obtained by the action of sunlight, while in the presence of polar substances only substitution derivatives of benzene would be produced.

Ethylene and chlorine, in the presence of steam, form ethylene chlorohydrine. Read<sup>28, 29</sup> obtained a large percentage of chloro- and bromohydrines due to the interaction of olefins with  $\text{Cl}_2$  or  $\text{Br}_2$  in aqueous solution. Francis<sup>11</sup> claimed that under conditions favoring ionization the initial stage in the addition of halogen to olefins must be the condensation of the positive ion of the halogen, which has a high energy content, with the organic molecule. Thus the production of ethylene dibromide has been expressed as consisting of three reactions:

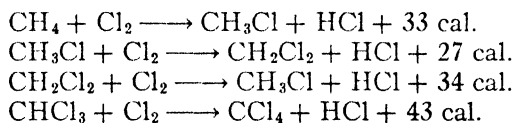
- (1)  $\text{C}_2\text{H}_4 \longrightarrow \text{CH}_2^+ - \text{CH}_2^+ : \text{Br}_2 \longrightarrow \text{Br}^+ + \text{Br}^-$  (activation reaction)
- (2)  $\text{Br}^+ + \text{CH}_2^+ - \text{CH}_2^+ \longrightarrow \text{BrCH}_2 - \text{CH}_2^+$  (reaction of the first ion)
- (3)  $\text{BrCH}_2 - \text{CH}_2^+ + \text{Br}^- \longrightarrow \text{BrCH}_2 - \text{CH}_2\text{Br}$  (reaction of the second ion)

If water is present, bromohydrine would be formed instead of ethylene dibromide because of the OH ions in the water, according to the equation:

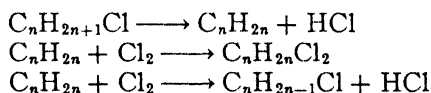


Because of the abundance of simple paraffin hydrocarbons and the small number of modes of chemical attack to which saturated hydrocarbons are susceptible, substitution reactions with halogens are of importance. The following points require consideration in the chlorination of paraffins.

(1) The reactions involved are highly exothermic. Approximate values for heats set free by the chlorination of methane and its chlorinated derivatives at  $400^\circ$  in the gaseous phase have been given by Jones, Allison and Meighan.<sup>19</sup>



In the chlorination of homologs of methane excessive temperatures give rise to the formation of olefins according to the following reactions:



Saturation of an olefin double bond with  $\text{Cl}_2$  leads to the formation of trichlorides and other higher chlorides.

(2) The partially chlorinated derivatives may be chlorinated further.

(3) Isomeric chlorides having less economic significance may be obtained.

Primary chlorides are valuable for the production of alcohols and chlorinated solvents. While primary isomers are stable, the tertiary chlorides decompose readily. Primary chlorides resist thermal decomposition and hydrolysis by action of water much better than the secondary and especially the tertiary isomers. Likewise esters obtained from primary



alcohols are better solvents, for example for nitrocellulose, than those derived from the secondary isomers.

(4) The presence of free chlorine in the chlorination of methane causes a slower rate of the process than that observed for its homologs.

(5) Free chlorine should not be used in chlorination and HCl should be removed as rapidly as formed on account of the corrosive nature of these substances.

With respect to the mechanism by which chlorination of paraffins takes place, Aschan<sup>1</sup> and also Wertyporoch<sup>33</sup> supported the theory of carbon skeleton rearrangement during the chlorination of *n*-pentane, while Hass and Weber's<sup>16</sup> work showed conclusively that no significant carbon skeleton rearrangement occurs in the chlorination of normal and isopentane. Hass, McBee and Weber<sup>17</sup> deduced from their investigation that hydrogen atoms are always substituted at the rates : tertiary : secondary : primary = 4.43 : 3.25 : 1.00 (for the reaction in vapor phase at 300°). This statement is contradictory to the assertion made by Ayres,<sup>2</sup> as well as one by Clark,<sup>5</sup> in which these investigators claimed that all the hydrogen atoms are replaced at equal rates by chlorine and that the composition of the chlorides may be derived from the number of hydrogen atoms in the various positions. Thus in *n*-pentane there are 6 primary hydrogen atoms and 6 secondary hydrogen atoms, and therefore in the chlorination 50 per cent primary and 50 per cent secondary isomers should be expected (48 per cent primary and 52 per cent secondary were obtained experimentally).

From the experiments on chlorination it has been deduced that moisture, carbon surfaces, light, etc., do not affect appreciably the relative rates of primary, secondary and tertiary substitutions, and that the reaction mechanism appears to be the same whether chains are initiated by catalysts at the carbon surface, by thermal association of Cl<sub>2</sub> molecules, or by adsorption of photons. It has been found that liquid-phase chlorination gives rates of primary, secondary and tertiary substitutions which in the case of the vapor phase are obtained at much higher temperatures. Chlorination in the vapor phase apparently suggests that the presence of Cl atoms on a carbon atom hinders further reaction upon that carbon atom during the second substitution.

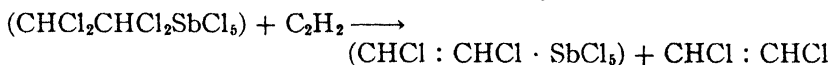
Muskat and Northrup<sup>23</sup> state that relatively small amounts of dichlorides are obtained in which two chlorine atoms are attached to the same carbon atom. In general, halogen atoms are considered as highly negative and the presence of a negative group usually activates the other atoms or groups attached to the same carbon atom. Such negative groups as phenyl or carboxyl will activate hydrogen atoms for chlorination. In the case of ethyl benzene there is a strong tendency to chlorinate, chiefly in the  $\alpha$ -position, and substitution in the  $\beta$ -position has been found to amount to 10 per cent at room temperature and 45 per cent at 500°, whereas it has been estimated that a non-selective chlorination would require a yield of 60 per cent  $\beta$ -phenylchloride. Complications may be introduced through an intramolecular rearrangement, should such occur through a parallel running dechlorination. Dechlorination in itself proceeds either by removal of chlorine in the form of HCl, sometimes followed by a varying degree of

condensation and/or polymerization of the resulting unsaturated residues, or by progressive substitution. The products of dechlorination may range from highly unsaturated substances to stable saturated oils. Dechlorination with alkali or metals having a high affinity for halogens is brought about at lower temperatures.

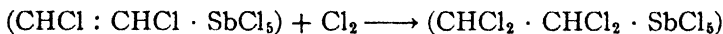
Friedel and Crafts observed (1877) the formation of oily polymers from amyl chloride by treatment with aluminum. This reaction was utilized for the purpose of synthesizing lubricating oils. Lubricating oils were prepared by the action of activated aluminum upon chlorinated fractions of "Kogasin" from low-pressure CO—H<sub>2</sub> synthesis at 130°. <sup>10, 20</sup> The oil obtained had high viscosity indices and was stable to oxidation. The AlCl<sub>3</sub> complex separated from the reaction products proved to be an active dechlorination catalyst. The activity of AlCl<sub>3</sub> as a dechlorination catalyst is emphasized in the case of coal-tar fractions dechlorinated to oils of a lubricating nature. <sup>7</sup> Hall, Wiggins and Nash, <sup>16</sup> dechlorinating chloroparaffins of low chlorine content, obtained products having good viscosity indices, but with very high carbon residues and dark in color. The dechlorination products of chlorinated middle oils of highly unsaturated character have been suggested as possible drying oils. <sup>12, 13, 14</sup>

Catalytic halogenation in industrial processes is rather widely practiced in the form of substitution, perhaps more so than the addition of halogen. The chlorination of acetylene, <sup>21</sup> using antimony pentachloride catalyst, is an example of the addition of halogen to an unsaturated linkage. The resulting addition compounds, dichlorethylene (CHCl : CHCl) and tetrachlorethane (CHCl<sub>2</sub> · CHCl<sub>2</sub>) are moderately stable. The latter is useful as a solvent. A better solvent is claimed to result from tetrachlorethane and water, using slaked lime. The process is said to occur in two stages:

(1) Tetrachlorethane is converted into dichlorethylene.



(2) Dichlorethylene is reconverted into tetrachlorethane.



Russakoff <sup>30</sup> recommends preparing monochloroacetic acid by bubbling chlorine gas through glacial acetic acid containing a small quantity (one per cent) of finely divided sulfur or phosphorus. Chlorination of simple paraffin hydrocarbons is of industrial importance. Chlorination of methane as a process resulting in an 80 per cent yield of carbon tetrachloride (N<sub>2</sub> : CH<sub>4</sub> : Cl<sub>2</sub> = 7 : 1 : 4) at 450° has been described by Boswell and McLaughlin. <sup>3</sup> This chlorination of the pentanes and butanes found in American natural gas is a process of industrial importance. Chlorination of paraffin hydrocarbons in the case of petroleum distillates proceeds smoothly at moderate temperatures either in gaseous or liquid phase, leading to mixtures of mono- and poly-chloroderivatives of varying complexity. The Standard Oil Co. of Indiana chlorinates 100,000 gallons of pentanes to monochloropentanes per day. Brooks and Humphrey <sup>4</sup> prepared a synthetic phenyl paraffin by treating chlorinated paraffin and benzene with anhydrous aluminum chlo-

ride. Conversion of benzene and toluene into chlor-derivatives by a combined action of 1.0 per cent iron and 0.1 per cent iodine<sup>8, 9</sup> and chlorination of the aliphatic radical in aromatic hydrocarbons to form benzyl and benzal chloride with phosphorus trichloride or sulfur chloride as catalysts (ultra-violet light has been used also to shorten the time of reactions) constitute processes of industrial significance.

In certain chlorinations, such as various bleaching processes, chlorine, alone or in a mixture with air, is passed upward through a tower containing active carbon in a granular form down which passes the liquid treated. Carbonyl chloride ( $\text{COCl}_2$ ) is a chlorinated product largely used in the synthetic organic industry, mostly in chemical warfare, under the name of phosgene, as well as an insecticide. According to Schiel,<sup>32</sup> the discoverer of phosgene, it is produced from equal volumes of carbon monoxide and chlorine exposed to bright sunlight or ultraviolet rays. The mixture of gases combines, however, in the absence of light, when passed through layers of activated charcoal at moderate temperature ( $100\text{--}125^\circ$ ) whereby one pound of active charcoal suffices for the manufacture of a ton of phosgene without reactivation of the catalyst.<sup>18</sup> Sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ), in the presence of carbon as catalyst, appears to be a valuable reagent in synthetic organic chemistry. The most active forms of carbon produce nearly 250 times their weight of sulfuryl chloride per hour.<sup>22, 27</sup>

Commercial halogenation in general is carried out with the assistance of substances acting as "chlorine carriers." In addition to active carbon,<sup>6</sup> metal chlorides as well as other chlorides, bromides and iodides are used with success for this type of catalytic reaction. Sabatier<sup>31</sup> classified the transporters of halogens thus:

Chlorine transporters: iodine, iodine-chlorine, sulfur, charcoal, bone charcoal,  $\text{MoCl}_5$ ,  $\text{PCl}_4$ ,  $\text{SbCl}_5$ ,  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{ThCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{V}_2\text{Cl}_5$ .

Bromine transporters: water-free bromides and chlorides and especially  $\text{I}_2$ ,  $\text{S}$ ,  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{FeCl}_3$ ,  $\text{FeBr}_3$ ,  $\text{HgCl}_2$ ,  $\text{HgBr}$ ,  $\text{Cl}_2\text{--Zn}$ .

Iodine transporters:  $\text{AlI}_3$ ,  $\text{FeCl}_3$ ,  $\text{FeI}_3$ ,  $\text{P}$ ,  $\text{Cl--I}_2$  and sub-iodic acid.

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## PART VI

### Catalytic Alkylation

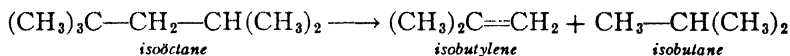
A catalytic reaction in which compounds containing alkyl groups react with alkyl-free compounds with a resulting change in the position of the alkyl groups, is called an alkylation process. Aliphatic hydrocarbons and aromatic amines may be alkylated by ethylene. Saturated hydrocarbons such as hexane are alkylated by olefins to alkyl-substituted paraffins. Alkyl groups may be introduced into the nucleus of aromatic compounds such as phenols, naphthalene, etc. Alcohols, cyclohexanol or ether may be used for the purpose of bringing the alkyl groups within the same molecule, but in another position. It is recognized that alkylation catalysts effect the combination of paraffins with olefins while these substances are *in statu nascendi*. Alkylation by means of an alkyl iodide or sulfate leads to the formation of an inorganic anion and an unstable organic cation, such as  $\text{CH}_3^+$  which acts as a cationoid reagent. In the meantime alkylation by means of an organo-metallic compound leads to the formation of metallic cations and is attributed to the formation of an organic anion such as  $\text{CH}_3^-$  acting as an anionoid reagent.

The alkylation of paraffins as well as naphthenes by olefins in the presence of  $\text{AlCl}_3$  has been interpreted by Ipatieff in the sense of intermediate formation of a complex compound between  $\text{AlCl}_3$  and the corresponding hydrocarbon, and further action of ethylene upon the complex compound to form an alkyl-substituted paraffin or naphthene. This mechanism of alkylation is of the type involved in catalytic chlorination reactions with  $\text{AlCl}_3$  as catalyst, wherein the Gustavson complex,  $\text{AlCl}_2(\text{C}_6\text{H}_5) \text{HCl}$ , is formed between  $\text{C}_6\text{H}_6$  and  $\text{AlCl}_3$ . Since the work of Balsohn<sup>1</sup> and Gustavson<sup>5, 6</sup> it has been known that aromatic hydrocarbons can be alkylated by olefins with  $\text{AlCl}_3$  as catalyst. Furthermore Friedel and Crafts' reaction established the fact that halide derivatives alkylate hydrocarbons with  $\text{AlCl}_3$  catalyst. Alkylation of paraffins was discovered by Ipatieff when he ascertained that a saturated hydrocarbon such as hexane is alkylated by ethylene at 60–70° and ordinary pressure over  $\text{AlCl}_3$  catalyst to form alkyl-substituted paraffins. Aluminum chloride has a tendency to break the paraffin chains into fragments. As the carbon-to-carbon links of paraffin and olefin chains are readily broken by  $\text{AlCl}_3$  this may lead to molecular degradation, such as cracking, isomeric changes, and other reactions.

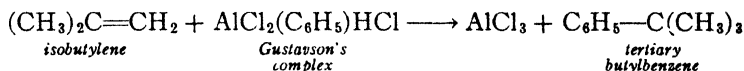
Alkylation is carried out with comparatively small amounts of  $\text{AlCl}_3$ , because the latter does not form a stable complex with the reaction product. Alkylations are sometimes reversible and are frequently accompanied by rearrangements in the carbon skeleton. The rearrangements accompanying the acylation of paraffins and cycloparaffins occur only in the alkyl chain

and act as a link between the two types. Orlov and Solodar<sup>16</sup> and Orlov and Vaisfeld<sup>17</sup> proved the reversibility of alkylation. Hoffmann, Farlow and Fuson<sup>7</sup> ascertained that the reversibility of alkylation may be shown by interconversion between mono- and poly-alkyl benzenes in the presence of  $\text{AlCl}_3$  and in the exchange of substituent groups. In general the reaction of  $\text{AlCl}_3$  with paraffins and cycloparaffins would not be completely described without mentioning the possibility that the paraffin may undergo a fission to a lower homolog and to an olefin, and that the latter may then condense with a second molecule of the original paraffin, or may itself polymerize, isomerize or become converted into an isomeric cycloparaffin.

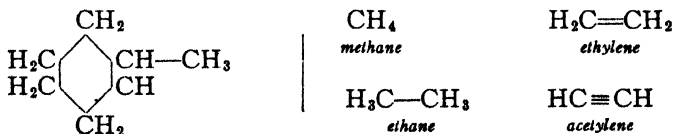
Alkylation permits the production of saturated hydrocarbons of an iso-structure, and thus is of industrial importance because it offers a process of synthesizing high-octane number paraffins. The catalytic alkylation of isobutane with ethylene and butylene gives a good yield of isoöctane of a high octane number. The reaction of direct alkylation carried out by Ipatieff and Grosse<sup>9</sup> at a temperature of  $150^\circ$ , 50 atmospheres' pressure, and 22 hours duration time, over a catalyst consisting of 15 g.  $\text{BF}_3$ , 7.5 g. HF and 5.0 g. Ni powder, gave 40 per cent of isopentane. It has been emphasized by Ipatieff that this reaction is superior to the Friedel and Crafts' reaction which requires preliminary preparation of alkyl halides; and it makes possible the introduction of radicals into molecules of certain hydrocarbons only through their agency. In certain cases alkylation is preceded by the decomposition of the hydrocarbon molecule, and in this destructive alkylation  $\text{AlCl}_3$  is a catalytic agent for both processes. It is possible to decompose the high molecular weight hydrocarbons and to alkylate the hydrocarbon resulting from the decomposition by the olefin. Such is the case with isoöctane obtained by reduction of diisobutylene which is split by  $\text{AlCl}_3$  according to the equation:



followed by the alkylation of isobutylene with benzene by  $\text{AlCl}_3$ :

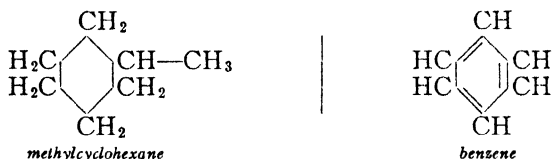


Alkylation of a six-membered cycloparaffin or cycloölefin ring yields not only the corresponding aromatics, but also end products resulting from either C—C or C—H breaks in the side chain alone, without being accompanied by a change in the ring structure. The simple hydrocarbon methylcyclohexane severs the C—C bond between the side chain and the ring to form a methyl radical which then hydrogenates to methane. The remaining radical undergoes further reaction to form ethylene and acetylene.

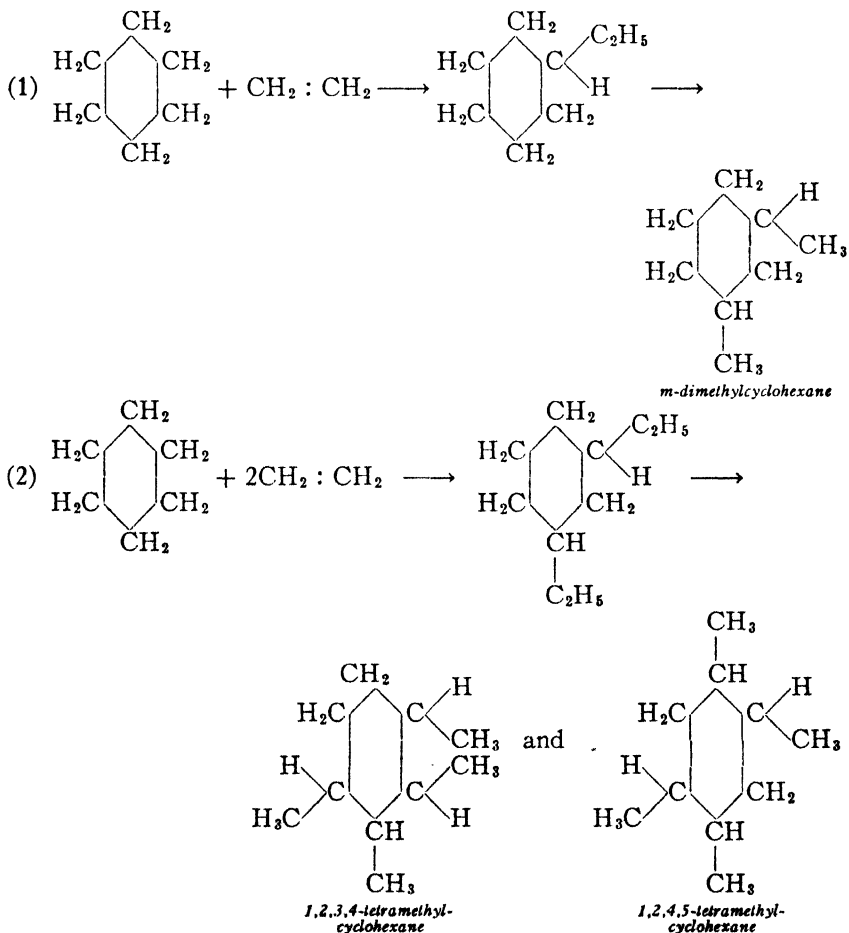


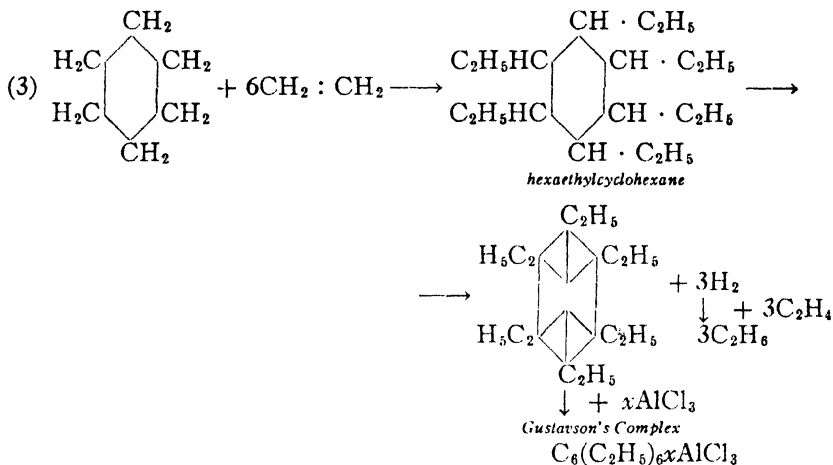
The alkylated and hydrogenated cyclic hydrocarbon yields products

formed not only by dehydrogenation of the ring or severance of bonds in the side chain, but by a combination of both mechanisms. For example, C—C linkages may be broken in the side chain at the same time that C—H bonds in the ring are being severed; thus methylcyclohexane on dehydrogenation may split off its CH<sub>3</sub> group, forming benzene. The intermediate product is CH<sub>3</sub> from the C—C break in the side chain.

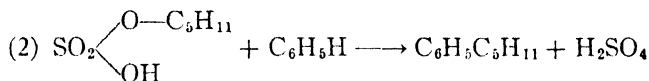
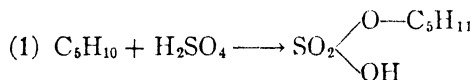


Alkylation of cyclohexane with ethylene in the presence of AlCl<sub>3</sub> to form *m*-dimethyl- and tetramethylcyclohexane has been described by Ipatieff, Komarewsky and Grosse<sup>11</sup> as consisting of three parts including isomerization.

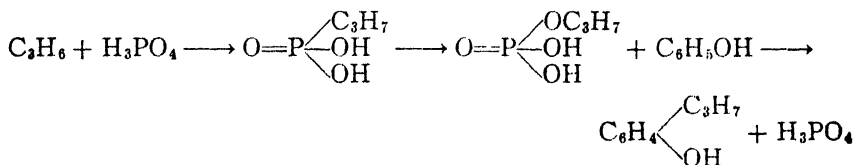




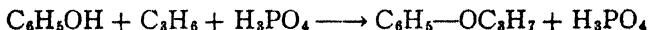
Spilker's<sup>19</sup> and Brochet's<sup>3</sup> studies, indicating that a hydrocarbon containing a double bond may condense with aromatic hydrocarbons (hexene + benzene  $\xrightarrow{\text{strong H}_2\text{SO}_4}$  hexylbenzene), led to the recognition of alkylating aromatic hydrocarbons with olefins in the presence of  $\text{H}_2\text{SO}_4$  as a catalyst. Ipatieff<sup>8</sup> describes alkylation of amylene with benzene over sulfuric acid catalyst by the following reactions:



Thus it is seen that the function of the catalyst is either to accelerate the substitution of the hydrogen in the benzene ring or to render the hydrogen atom in the benzene ring more mobile. As an intermediate step in the reaction an ester is formed between the catalyst and the olefin. Alkylation of phenol in the presence of aluminum chloride catalyst has been carried out by Ipatieff, Orlov and Razuvaev<sup>12, 13</sup> but recently Ipatieff found that alkylation of phenols by olefins proceeds so easily over phosphoric acid as catalyst, that even olefins diluted with other hydrocarbons may be used. Alkylation of phenol by olefins with phosphoric acid catalyst has been expressed by Ipatieff in the scheme:



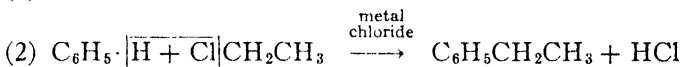
with the simultaneous formation of phenyl ether according to the equation:



Experimental evidence points to the fact that phosphoric acid catalyst has an advantage over sulfuric acid catalyst in that no sulfur acids and less tarry material are formed.

Alkylation of aromatic and heterocyclic rings has been found to be frequently accompanied by a rearrangement of the alkyl group, thereby producing a branching of the chain, often the maximum possible branching. Besides aluminum chloride other catalysts active in hydrocarbon reactions are  $\text{BeCl}_2$ ,  $\text{BF}_3$ ,  $\text{TiCl}_4$ ,  $\text{ZrCl}_4$ ,  $\text{HfCl}_4$ ,  $\text{ThCl}_4$ ,  $\text{NbCl}_5$ , and  $\text{TaCl}_5$ . Ethylation of benzene with ethylene by means of these catalysts has been described by Grosse and Ipatieff.<sup>4</sup> In each case a mixture of mono- and poly-ethyl benzenes up to hexaethyl benzene are formed. The amount of different ethyl benzenes depends on the catalyst used in the catalytic alkylation, the ratio of amounts of ethylene and benzene used, time of reaction, temperature, and pressure. Most of the catalysts, even under conditions favoring the formation of monoethyl benzene, produce simultaneously the higher alkylated products.

While one molecule of aluminum chloride, according to the investigation of Kurbatow,<sup>20</sup> converts 104 molecules of ethylene into alkylated benzene, the metal halides also behave as catalysts, each molecule converting only 50 molecules of ethylene into ethyl benzene.  $\text{TaCl}_5$  seems to be just as active as  $\text{AlCl}_3$ , while  $\text{ZrCl}_4$  is equal to or even better than the latter. As for  $\text{BeCl}_2$ , it was ascertained that it becomes active first at higher temperatures ( $200^\circ$ ). Among all the catalysts mentioned,  $\text{TiCl}_4$  appears to be the weakest. Grosse and Ipatieff state that for the catalytic action of halides the presence of hydrogen halide (mostly  $\text{HCl}$ ) is necessary. The action of hydrogen halides is expressed by the following reactions:



In case larger amounts of  $\text{HCl}$  are used the presence of ethyl chloride may be proved readily.

Ethylation of naphthalene to ethyl naphthalenes with  $\text{AlCl}_3$  and the use of ethyl benzene instead of ethylene as a source of ethyl groups have been carried out by Milligan and Reid.<sup>15</sup> The Rheinische Kampfer Fabrik A.-G.<sup>18</sup> also patented a process in which naphthalene is converted to poly-ethyl naphthalene by heating to  $250^\circ$  in an autoclave over activated tonsil under a pressure of 20–40 atmospheres of ethylene. Propylation of naphthalene using alkylated benzene as a source of propyl groups, whereby isopropyl groups are transferred from diisopropyl benzene to naphthalene by means of  $\text{AlCl}_3$  catalyst, has been investigated by Berry and Reid.<sup>2</sup>

Wulff<sup>21</sup> emphasized the fact that synthesis of lubricating oils may be effected by alkylation of aromatics. Ethylating naphthalene (700 g.) with ethylene under 80–85 atmospheres' pressure at  $240^\circ$  in the presence of 40 g. of  $\text{AlCl}_3$  catalyst he obtained an oil consisting largely of ethyl and diethyl naphthalene. Ipatieff, Corson and Pines<sup>10</sup> propylated naphthalene to isopropyl naphthalene using as catalyst 96-per cent  $\text{H}_2\text{SO}_4$ . Ipatieff, Pines and Komarewsky<sup>14</sup> effected alkylation of naphthalene to mono- and



diethyl naphthalenes by using 85-per cent  $\text{H}_3\text{PO}_4$  at  $300^\circ$ ; when using propylene they obtained, with the same catalyst, monopropyl naphthalene at a temperature as low as  $200^\circ$ .

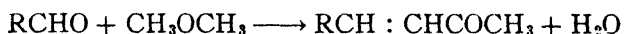
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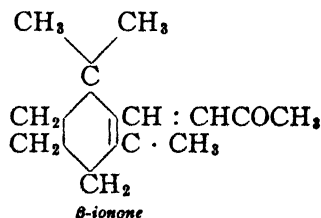
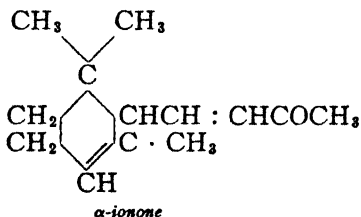
## PART VII

### Catalytic Condensation

Contrary to polymerization processes, in which molecules of the same kind combine to form larger units, condensation processes constitute a group of reactions in which different organic molecules become united. Numerous specific catalysts effect condensation of organic molecules, which often proceeds with elimination of either water or hydrochloric acid. A condensation process with elimination of water is, for example, that of an aldehyde or ketone with acetone according to the scheme:

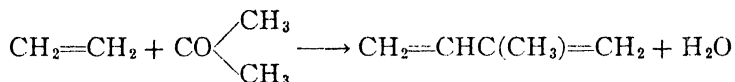


As shown by Claisen and Ponder,<sup>2</sup> using dilute alkali as catalyst, the unsaturated ketones obtained may be converted into derivatives of industrial value. Citral condensed with acetone over baryta solution gives pseudionone:  $(\text{CH}_3)_2\text{C} : \text{CH} \cdot \text{CH}_2\text{CH}_2 \cdot \text{C}(\text{CH}_3) : \text{CH} \cdot \text{CH} \cdot \text{CHCOCH}_3$ , which, when subjected to the catalytic action of dilute  $\text{H}_2\text{SO}_4$ , rearranges to form a mixture of two isomeric ring compounds,  $\alpha$ - and  $\beta$ -ionone of the structure:

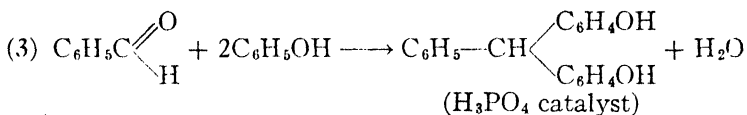
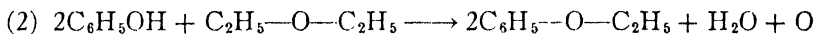
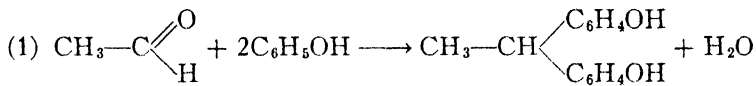


Both of these ketones are produced in large amounts, their fragrance resembling that of violets.<sup>16</sup>

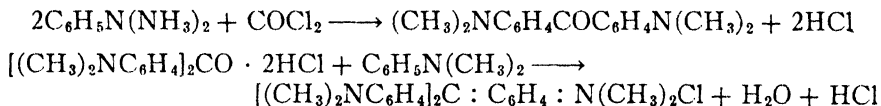
Condensation of ethylene and acetone to form isoprene proceeds with separation of water<sup>13</sup> according to the following scheme:



Condensation of acetaldehyde with phenol,<sup>16</sup> of ethyl ether with phenol,<sup>18</sup> as well as of benzaldehyde with phenol take place with the formation of water:



A separate class of condensation processes is that in which HCl is eliminated from the two combining organic molecules by means of the classical reagent  $\text{AlCl}_3$ . This method is known as the Friedel and Crafts method.<sup>6, 7</sup> An intermediate compound is formed between the catalyst and either one of the reacting substances; it is stable and has been isolated. In the case of acid chlorides a crystalline derivative  $(\text{KCl} \cdot \text{AlCl}_3)_2$  originates, and between the hydrocarbon and  $\text{AlCl}_3$  a complex of the structure  $(\text{C}_6\text{H}_6 \cdot \text{AlCl}_3)_2$  is formed. Friedel and Crafts' synthesis has been applied, for instance, in the preparation of anthraquinone by condensing phthalic anhydride with benzene in the presence of  $\text{AlCl}_3$  as catalyst. Methyl- and chloro-anthraquinones were produced from chlorobenzene or toluene and phthalic anhydride. An important application of the same synthesis is in the industrial production of aromatic ketones, by use of carbonyl chloride as organic halide, the crystal violet dyestuff being formed thereby according to the equation:

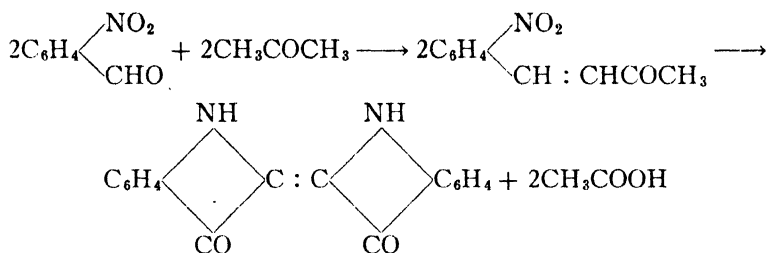


The Fischer-Tropsch process<sup>5</sup> converts olefinic hydrocarbons produced from water gas into useful lubricating oils either by auto-condensation with  $\text{AlCl}_3$  catalyst or by first chlorinating the fractions and then subjecting them to the Friedel and Crafts condensation, either alone or with commercial xylene or other aromatic hydrocarbons.<sup>11, 12</sup> Lubricating oils synthesized by condensation reactions possess in general a high proportion of aromatic structure in their molecular constitution, and have rather poor viscosity indices with relatively high viscosity and specific gravity for a relatively low boiling range.

The condensation of olefins with benzenoid hydrocarbons to produce

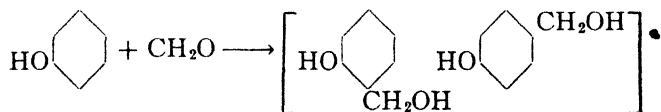
ethyl benzene, using  $\text{AlCl}_3$  as catalyst, has been another instance in which Friedel and Crafts' method proved successful. Condensation of propylene and benzene to di- and tri-isopropyl benzenes has been used by Ipatieff<sup>17</sup> for the production of alkyl-aryl hydrocarbons with high anti-knock ratings. In this process benzene hydrocarbons are treated with gaseous olefins from petroleum gases, using  $\text{H}_2\text{SO}_4$  as catalyst; the products are then condensed with more benzene or other aromatic hydrocarbons in the presence of  $\text{AlCl}_3$  catalyst.

Among other industrial processes based on catalytic condensation may be mentioned the manufacture of synthetic indigo discovered by Baeyer and Drewsen.<sup>1</sup> *Ortho*-nitrobenzaldehyde is condensed with acetone by means of dilute caustic soda.

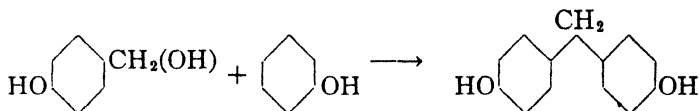


Condensation of phenols, urea and other substances with aldehydes in the presence of basic or sometimes acid catalysts often leads to resin formation. Plastics and lacquers have as a base resins of the Bakelite type. Three types of Bakelite were differentiated according to their solubility and fusibility. Morgan<sup>14</sup> recently suggested as a mechanism for the phenol-formaldehyde condensation one consisting of several steps:

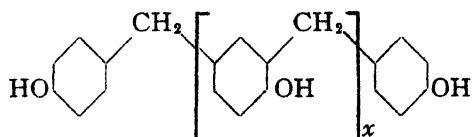
- (1) Formation of *o*- and *p*-hydroxybenzyl alcohols:



- (2) Formation of dihydroxydiphenylmethanes by a further addition of phenol:



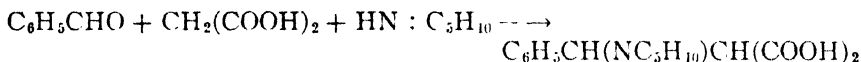
- (3) Formation of long-chain compounds, such as the following:



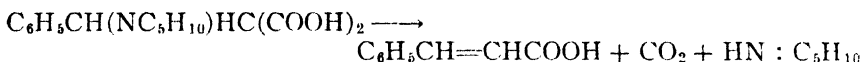
which may occur in many isomeric forms.

In certain processes catalytic condensations are carried out with organic compounds as catalysts. Catalysis of methylene condensations by means of diethylamine takes place with piperidine as catalyst. An intermediate compound is formed between the catalyzing base and one of the reaction partners.<sup>8, 9, 10</sup>

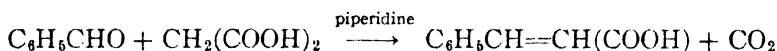
It has been found<sup>15</sup> that benzaldehyde and malonic acid undergo condensation with piperidine as catalyst at ordinary temperatures. The piperidine enters into a complex according to the following equation:



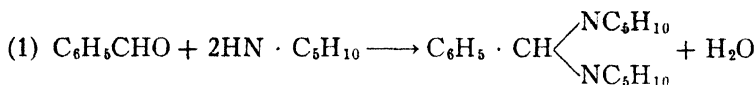
This substance decomposes on heating to cinnamic acid and  $\text{CO}_2$ , whereby piperidine is set free:



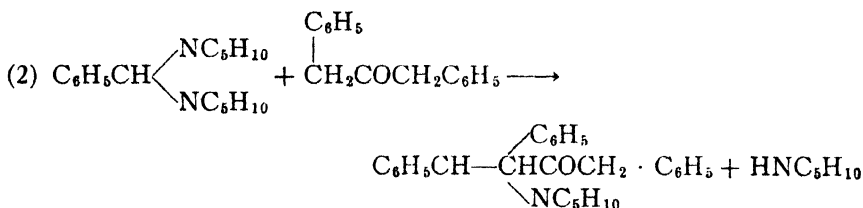
If the reaction is carried out at once by heating the components, then cinnamic acid is formed directly:



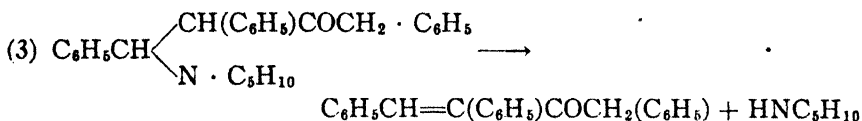
Dilthey and Nagel<sup>3</sup> and Dilthey and Stalman<sup>4</sup> investigated the condensation of benzaldehyde with dibenzylketone in the presence of piperidine as catalyst. Three stages were distinguished in this catalysis:



with formation of an intermediate compound between the aldehyde molecule and two piperidine molecules.



The piperidine molecule is regenerated or a molecule of dibenzylketone is added to the complex.



Thus by splitting off a second piperidine molecule a complete regeneration of the catalyst is effected by an acid treatment, and a double bond is thus formed between the original aldehyde group of benzaldehyde and the

methylene group of dibenzyl ketone. The reaction velocity depends on the stability of the intermediary aldehyde-dipiperidine complex. The less stable it is the faster the condensation takes place.

Scheiber and Sändig<sup>15a</sup> distinguish the following synthetic plastics obtained by condensation or polymerization reactions:

- (1) Coumarone resins which are produced by polymerization of certain fractions of solvent naphtha, using sulfuric acid.
- (2) Aldehyde resins produced from acetaldehyde and croton aldehyde, using as condensing agents alkali and sulfuric acid.
- (3) Phenol-aldehyde resins produced from phenols and aldehydes with various condensing agents determining their properties.
- (4) Urea-formaldehyde resins obtained by using acids or bases as condensing agents.

Resins of the "glyptol" type are reaction products of condensed phthalic anhydride and polyhydric alcohols.

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## PART VIII

### CATALYTIC POLYMERIZATION

#### Concepts Associated with the Polymerization Process

Berzelius<sup>3, 61</sup> the first to interpret polymerization processes, conceived the idea that polymerized products, *i.e.*, polymers, are substances having an equal percentage composition, but various molecular weights. Holleman<sup>62</sup> described polymerization as a process in which two or more molecules of a substance are linked together in such a manner that they may be regenerated. Staudinger<sup>79, 80</sup> criticizing this concept, states that this criterion is not at all essential for a polymerization process, because the composition may show different degrees of decomposition without depolymerization to the monomolecular body. In other words, polymerization is not always accompanied by depolymerization, and even if it is, the depolymerization does not necessarily regenerate the primary substance. The reversibility may be incomplete. Staudinger's interpretation of polymerization postulates a combination of two or more molecules of one compound to form a product of the same percentage composition, but with a greater

molecular weight. An attempt<sup>29</sup> was made to differentiate polymerization as physical polymorphism (as in the case of sulfur) from polymerism, and from this point of view polymerization has been considered as a process in which structural-chemical changes are involved. Polymerization processes have been assumed to be similar to isomerization processes in which the participating substance is definitely changed. Structural-chemical changes impart special characteristics to the polymerizate and are reflected in the physico-chemical variability of its properties. The concept of polymerization may not always be distinguished from that of association. If the primary particles are considered as chemical molecules, then for a double molecular weight a transition by a change of state of the aggregate may be involved, and the formation of such molecular aggregates would follow the laws of crystallization from saturated solutions.

This point of view has been anticipated by Hess<sup>31</sup> in the discussion of whether cellulose is a polymerized glucose anhydride (a certain number of glucose anhydride molecules are combined with one another through oxygen bridges), a polymerized cellobiose anhydride, or finally an association of trisaccharide anhydride. He states that it is immaterial whether the molecule is of the size of glucose anhydride, biosan, or trihexosan, because if the molecule is larger than a glucosan then both polymerization and association can be accepted as an explanation of the transition to a high molecular state.

That the polymerization process is not an association phenomenon but rather chemical in nature and dependent on hydrolysis, as well as on condensation, has been stated by Konrad, Bächle and Signer.<sup>45</sup> In the large molecules of silicic ester, atomic union takes place by normal covalent linkings between definite atoms. Treatment of one molecule of methyl *ortho*-silicate with 0.5 mol of water leads to the almost exclusive formation of the disilicic ester  $[(\text{MeO})_3\text{Si}]_2$ . The use of one molecule of water produces practically a quantitative yield of a polymeric silicic ester of molecular weight  $\sim 10,000$ . It is assumed that the action of water is purely hydrolytic and leads to an infinite series of consecutive reactions ultimately producing homogeneous molecules of the type:  $(\text{MeO})_3\text{SiO}[\text{Si}(\text{OMe})_2 \cdot \text{O}]_x\text{Si}(\text{OMe})_3$ .

While Meyer<sup>60</sup> expressed his belief that polymerization is due to the action of intermolecular cohesive forces, Staudinger<sup>86</sup> supposed that in a polymerizate all atoms are joined by ordinary covalent linkings, and it is therefore not an associated group of units joined together by a separate cohesive force.

With respect to the product of a polymerization process, it appeared essential to distinguish between chemical and physical polymerization. Chemical polymerization is concerned with an equilibrium of a small part of a substance in a colloidal state and a large part in molecular solution. The opposite is true for the physical type of polymerization. Certain properties of the polymerizate, such as plasticity and elasticity, especially significant in products obtained by industrial polymerization processes, imply the physical type of polymerization. On the other hand, at proper

temperature and pressure, only a pure chemical polymerization may be involved, and the polymerized products resulting from it are of the type of molecular aggregates rather than colloidal particles. A slow process taking place at low temperatures favors the production of a polymerizate with pure colloidal properties. Thus very often the complexity in the behavior of natural and synthetic polymerization products may be traced back not to the difference in the ingredients making up the mixture, but to the colloidal state of substances in the polymerizate, due to physical conditions under which it was formed.

With respect to types of polymerization, the following two were emphasized by Kronstein:<sup>50</sup> the first comprises processes in which the monomer substance gradually becomes viscous and finally changes into a high polymer (mesomorphic); the second is one in which the monomer polymerizes without changing its consistency and the separated polymer is entymorphic. As examples are cited conversion of acrylic acid into polyacrylic acid and of cyanic acid into polycyanic acid (cyamelide). However, according to Frost's unpublished data,<sup>25, 87</sup> the idea of Kronstein that intermediate products of styrol originating in the polymer process change gradually into solid polystyrol is incorrect, as the solution becomes viscous as a result of the presence of thread-like molecules. According to Frost's observations, in the polymerization of styrol at 60°, molecules of the same length originate at the beginning, as well as at the end of the process, and the polymer remains dissolved in the monomer.

It has been assumed by Staudinger that in some polymerization processes the molecules are bound together by normal covalences and the depolymerization or decomposition of the polymer molecules into the monomers depends on the stability of the polymerization product ("normal" products). In other polymerization products called "coördinative" the basic molecules linked together by coördinative valences are not stable and depolymerize readily. The normal polymerization process was subdivided by Staudinger into true and condensation polymerization processes. In the first type the polymerizate has the same binding of atoms as the base molecule (triphenylmethyl to hexaphenylethane; formaldehyde to trioxymethylene; ketenes to cyclobutandion). In the condensation polymerization processes the formation of the polymer from the monomers presumes an atom displacement—a removal of hydrogen—and therefore the previous binding of atoms is not maintained (polymerization of formaldehyde to glycolaldehyde and sugars, polymerization of styrol to distyrol). This polymerization is similar to true condensation processes, in which molecules of various composition are connected in an analogous manner. Thus when the previous bindings of atoms in the monomer are not maintained in the polymer, the product is referred to as a condensed polymerizate.

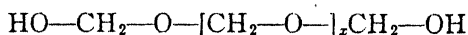
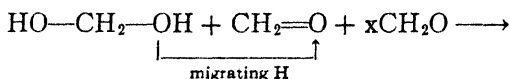
The highly polymeric substances originate synthetically only by true polymerization because the condensation ability decreases with increase in size of the molecule and finally stops, so that a low molecular weight polymer results. The true polymerization process is illustrated as follows:



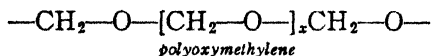
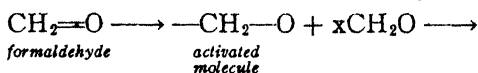


occurs in a solid state, so that one glucose group is intercalated in the crystal lattice and the binding is effected through main valences. The growth of the crystallite proceeds hand in hand with the growth of the thread molecule. The discontinuation of a chain takes place when a catalyst and high temperature are used rather than in the absence of these factors, for under these conditions of polymerization not the primary particles of ordinary colloids, but new colloids with smaller molecules, classified by Staudinger as hemi-colloids, are formed. Their physical properties stand between those of low molecular weight organic substances and those of high molecular weight colloids, *i.e.*, eucolloids (Ostwald<sup>69</sup>) or macro-molecule colloids (Staudinger<sup>65</sup>). Staudinger assumes that the longest molecules may be formed at the lowest possible temperatures and without additions, so that the chain reactions proceed undisturbed. Under these conditions the molecules formed may develop surprising length and acquire peculiar colloidal properties. The highest degree of polymerization of molecules of polystyrols is estimated at 6000, and the length of their thread molecules is calculated as  $1.5\mu$ . Much higher molecular products cannot be obtained because still longer thread molecules cease to be stable at room temperature.

It is believed that caoutchouc may be formed by linking single-thread molecules to three-dimensional molecules. If the linking occurs only at a few places, then the products swell very greatly, which is the case with weakly vulcanized caoutchouc. In the case of hard rubber, a strong linking takes place and the solvent does not penetrate into the substance, so that swelling is stopped.<sup>62</sup> The transition of  $\alpha$ -caoutchouc into  $\beta$ -caoutchouc is based on the formation of three-dimensional molecules and the soluble caoutchouc is thereby converted into the insoluble form. Some substances are suitable for polymerization as well as for polycondensation, for example, formaldehyde, oxystyrol, vinyl alcohol and unsaturated fatty acids. However, essential differences are recognized between the two kinds of reactions.<sup>47</sup> In the case of polymerization and poly-condensation, in addition to the formation of thread-like polymer molecules of various degrees of polymerization ("linear colloids" according to Staudinger), processes leading to ring formation and open chain branching or to partial net formation between single thread molecules, finally forming round macro-molecules (sphero-colloids), have to be considered. In the conversion of formaldehyde, the condensation-polymerization:

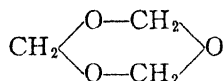


is differentiated from the chain polymerization:

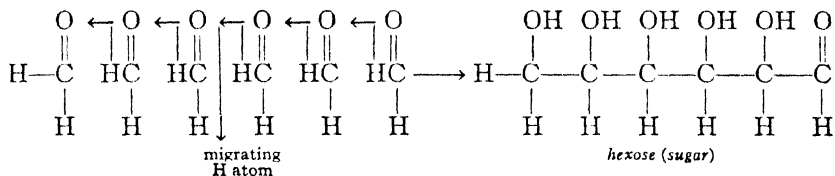


Thus low- and high-molecular weight polyoxymethylene of a thread-like or

branched form or low-molecular weight rings such as, for example, trioxymethylene are formed:

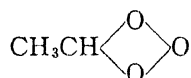


An interesting form of formaldehyde linking represents condensation-polymerization proceeding under the influence of weak alkalis:



An amount of sugar is thus formed from the aldehyde through aldol condensation. By a conversion of formaldehyde with phenol according to the type of condensation depending upon the ratio (phenol: formaldehyde) low- or high-molecular weight Novo-lacquers are formed; with an excess of formaldehyde, Resitol and finally Resit<sup>51</sup> are obtained.

Cuthbertson, Gee and Rideal<sup>27a</sup> assume that polymerization reactions are based on catalytic action of chain-producing peroxides. They discuss the polymerization of vinyl acetate. It has been found that commercial vinyl acetate may contain traces of acetaldehyde which forms, in the presence of air, a peroxide, possibly of the formula:



The presence of the peroxide has been proved in several samples of vinyl acetate which polymerized readily and the greater its concentration the more marked its polymerization ability. The compound may be separated with good fractionating columns, but not by a careful vacuum distillation. The influence of sodium hydroxide upon moist vinyl acetate is based on its saponification to vinyl alcohol which is tautomeric with acetaldehyde. With regard to the aldehyde-free vinyl acetate, it was observed that polymerization failed to take place even at 100° and in the presence of oxygen (prior to heating, the samples are shaken for two weeks with oxygen).

The difference between polymerization and condensation is that in the latter case the stepwise growth of the molecule may occur as a result of splitting off of small molecules, such as water, ammonia, etc. Condensation reactions do not form chains of appreciable length. There is no great difference between the velocity of the first step and that of the following steps. It is presumed that no intermediate existence of free radicals or of highly activated states is to be postulated. Some condensation reactions lead to the formation of unbranched chains. In the case of polycondensation no essential difference between the velocity of formation of the nuclei and the chain growth may be assumed.

Thermal non-catalytic polymerization must be distinguished from cata-

lytic polymerization. In the latter a line of demarcation is drawn by Ipatieff<sup>36</sup> and Ipatieff and Pines<sup>37</sup> between "true" polymerization and "conjunct" or "bound" polymerization of olefins. By true polymerization is understood a process forming only dimers, trimers and polymeric products. "Bound" polymerization is on the contrary that in which saturated and unsaturated paraffins are formed in addition to cyclic compounds. Ipatieff, studying the polymerization of olefins by the action of sulfuric acid, ascertained that under the influence of a dilute acid a "true" polymerization takes place in which polymers of initial olefins are formed, whereas from the initial alkyl sulfuric acid esters longer chains are formed, with splitting off of  $H_2SO_4$  and combination of the alkyl residue. The polymerization with concentrated  $H_2SO_4$  is accompanied by other reactions, namely, depolymerization, cyclization, dehydrogenation, hydrogenation and isomerization, and therefore corresponds to the type of "conjugated" polymerization. The initial reaction is broken in a series of reactions and from the resulting alkyl esters, open chain olefins and cyclic hydrocarbons are formed, which undergo intermolecular hydrogenation. By a further dehydrogenation of the cycloparaffins a cycloolefin and hydrogen are formed which, in their turn, are used for the hydrogenation of olefins to paraffins.

With dilute acids and under mild conditions true polymerization is favored; high temperatures and pressures induce conjunct polymerization.

### Types of Polymerization Processes

Polymer products may be prepared from mono- or poly-saturated compounds. Likewise, substances may be used which acquire polymerization ability through secondary reactions. Most hydrocarbon compounds have no polar antipodes between their component atoms, and are therefore homopolar, such as for example, hydrocarbons, chlor- derivatives, esters, ethers, and partially also alcohols. A different relationship exists in the case of heteropolar organic compounds such as true acids, bases and salts. It has been emphasized that, by using homo- as well as heteropolar organic compounds in the polymerization process, the physical properties of the polymers formed may be greatly influenced. Natural and artificial products may serve as examples for the essentially different physical properties

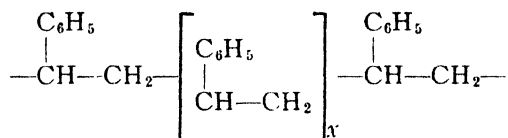
Table 1. Types of Polymerization.

Type	——Homo- and Heteropolar High Molecular Weight Polymer—— Compounds and Derivatives	
	Natural	Synthetic
Isopolymerization.	Rubber. Chlor-rubber. Cellulose acetate. Cellulose. Starch. Albumin.	Polystyrene. Polyvinyl chloride. Polyvinyl acetate. Polyoxymethylene. Polyvinyl alcohol. Polyacrylic acid.
Mixed polymerization.	Cellulose mixed ester and ether.	Polyvinyl acetate-polyvinyl chloride. Polystyrene-polydivinyl benzene. Polyvinyl chloride-poly acrylic acid ester. Polystyrene-polyacrylic nitrile.
Heteropolymerization.	Cellulose-xanthogenate solution.	Polyvinyl acetate-maleic acid. Stilbene-maleic anhydride.
Dehydro- or hydro- polymerization.	Biologic processes, oil drying.	Resin formation from saturated and un- saturated aliphatic and aromatic com- pounds, <i>e.g.</i> , tar oils.

of the two classes of compounds in the monomer as well as the polymer state. Such high molecular weight homopolar compounds as caoutchouc, cellulose acetate, polystyrene and polyvinyl chloride dissolve in organic solvents, but do not dissolve in water, whereas heteropolar high molecular weight compounds, such as albumins or polyacrylic acid, are brought into solution with water.

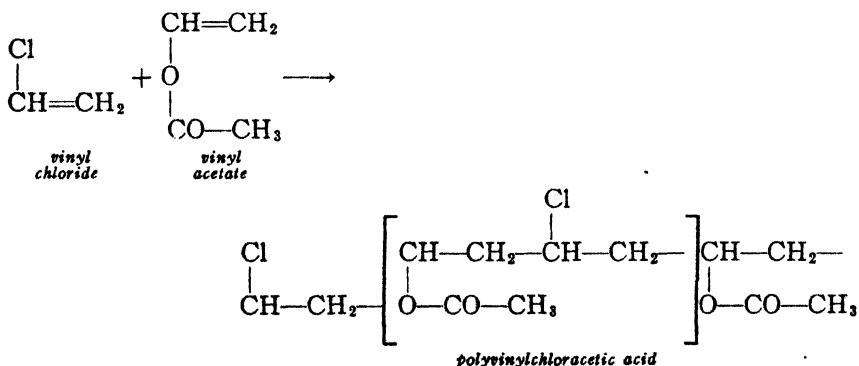
From this point of view natural and synthetic high molecular weight compounds formed by the following types of polymerization have been differentiated.

Ordinary polymerization is the conversion of unified products able to polymerize into polymers. Homogeneous branched or round molecules are linked one to another within the chain-line, for example, polystyrene:



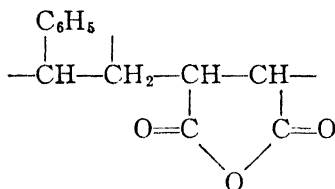
When the physical properties of the polymer compounds correspond to those of the initial molecules, but are determined chiefly by the structure and the size of the polymer molecules, the process in which the isopolymer products originate is referred to as isopolymerization.

Not only may high-polymer compounds be formed by polymerization of unsaturated molecules, but two or more different molecules may combine to form one new polymer molecule. The structure of this molecule is of the chain type, and the sequence within it is changeable. This process is designated as mixed polymerization. The properties of the polymer product and those of a mixture of polymers are not the same. A new homogeneous substance is formed and a series of new combinations with new specific properties is made possible, so that such synthetic products may find application in cases where isopolymer products prove to be ineffective. In normal mixed polymerization two or more of the initial molecules combine, but each in itself is able to polymerize. Examples of mixed polymerization that have been mentioned are acrylic nitrile and styrene, monomer styrene and divinyl benzene or monomer vinyl acetate and vinyl chloride. The combining process of the latter mixture proceeds as follows:



The sequence within the mixed polymer products may be altered. Irregularities in composition are sure to appear if the components have different polymerizing properties. The homogeneity of the products obtained may be regulated by continuous addition of the component most readily polymerized. The combining of two molecules structurally identical but of very different polymerization abilities constitutes a case of anomalous mixed polymerization, designated as heteropolymerization by Wagner-Jauregg.<sup>104</sup> It is possible, however, to combine a non-polymerizable component in a mixture with a polymerizable component in order to form a homogeneous polymer product. It has been pointed out<sup>104</sup> that substances unsuitable for isopolymerization are suitable for heteropolymerization. On the other hand not all unsaturated compounds are suited for heteropolymerization. The substitutes at the ethylene bond strongly affect processes taking place there. Unsaturated compounds which in themselves do not polymerize are, *e.g.*, crotonic acid, maleic acid and their derivatives.

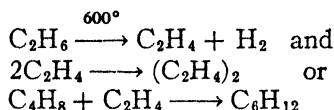
Maleic anhydride forms with styrene a mixed polymerizate of the structure:



Heteropolymers include those compounds which originate from ethylene or butadiene hydrocarbons (for example, isoprene) by the action of  $\text{SO}_2$ . These polymer sulfonates have extremely high molecular weight (Staudinger). In the case of poly-condensation processes, a distinction is made between iso-poly-condensation (condensation of oxyacids according to Carothers) and heteropoly-condensation (condensation of formaldehyde with phenol).

By the action of such chemical agents as  $\text{H}_2\text{SO}_4$ ,  $\text{AlCl}_3$ , or  $\text{ZnCl}_2$  upon saturated or unsaturated aliphatic or aromatic hydrocarbons, for example, petroleum, cracking benzene and tar oil, several reactions may take place simultaneously. Often the corresponding compounds undergo first dehydrogenation, then polymerization, and finally hydrogenation. These processes, which finally may lead to the formation of resin or asphalt-like substances, often occur in distillations even in the absence of oxygen. The resin-like substances obtained in these dehydro- and hydro-polymerization processes are believed not to be "true" polymers of the olefins, originally present, but products resulting from cracking and dehydrogenation processes accompanied by polymerization.

Saturated hydrocarbons of low molecular weight, when heated, readily decompose into unsaturated hydrocarbons of low molecular weight, and hydrogen. The composition of the products thus formed is influenced by the pressure. By thermal decomposition of petroleum under suitable conditions, monoolefins and diolefins are formed. These unsaturated hydrocarbons polymerize. Thus, reactions like



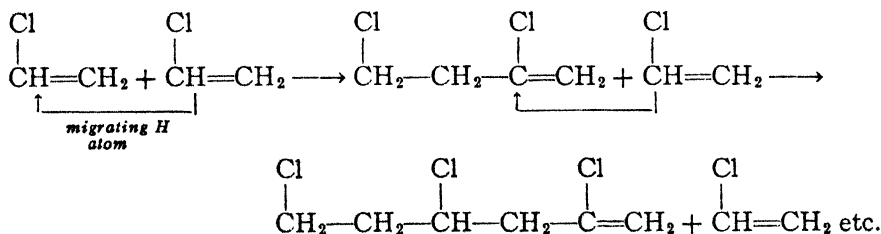
take place, leading to the formation of unsaturated polymers.

From methane and ethane, polybutadiene and polyindene, containing resins, are obtained. In these resinification processes, effected by dehydro- and hydropolymerization of low molecular weight organic compounds, a hydrogen migration takes place, a part of the substance concerned being dehydrogenated; by the splitting off of hydrogen, unsaturated groups not before present induce polymerization under the influence of catalysts in the system. The polymers thus formed may be unsaturated, dehydro-polymers, as well as hydrogenated products. Dehydro-hydropolymerization has been studied with respect to low molecular weight compounds, but little work has been done on the high molecular weight products. It has been established also that polymerization processes of this order sometimes do not lead to a precipitation of resin-like substances, but rather result in a thickening of the initial material. The polymer substances formed on distillation are often undesirable side products. A combination of processes of definite nature occurring in correct sequence may prove of great significance in the conversion of cheap, low molecular hydrocarbons into high molecular, light, elastic solids and film-forming products, due to polymerization in the final step.

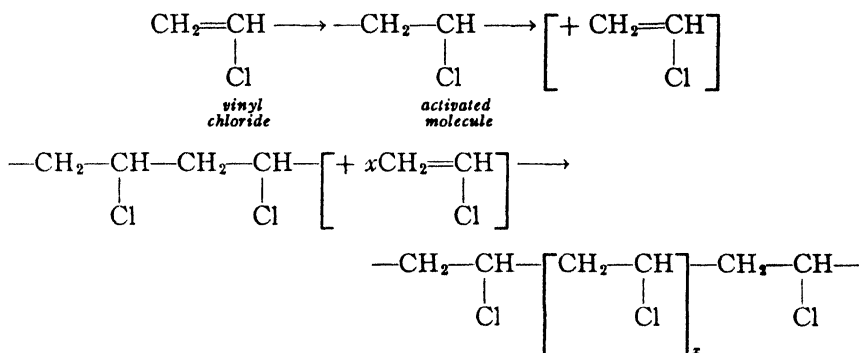
### Mechanism of Polymerization with Respect to the Kind of Compounds Polymerized

The process of polymerization takes its own course, originating in saturation of free valences or residual valences, conversion of unstable ring systems or in hydrogen migration (dehydrogenation polymerization and condensation-polymerization). Specially inclined to polymerize are compounds with double bonds  $\text{C}=\text{C}$ ,  $\text{C}=\text{O}$ ,  $\text{C}=\text{S}$ , as well as  $\text{C}=\text{N}$ , and compounds such as ethylene oxide, peroxides, ozonides and lactones.

The poly-condensation process (formation of poly-esters from oxy-acids) shows in contrast to condensation reactions no splitting off of water, ammonia,  $\text{H}_2\text{S}$ ,  $\text{HCl}$  or  $\text{HBr}$ , but only a migration of hydrogen within the molecules. In the case of the poly-condensation of vinyl chloride, the unsaturated molecule joins another molecule by hydrogen migration, and continuation of such a reaction results in the formation of polymer products:



Polymerization may occur without migration of hydrogen or other atoms as well as without splitting off of groups, simply through a chain mechanism. This reaction is comparable to the Cl-detonating gas chain reaction. Single molecules of the corresponding unsaturated compounds are activated and this enables them to add new molecules. The chain polymerization of vinyl chloride may be expressed as follows:



Therefore new molecules with active end-groups are formed and the polymerization proceeds until, through a side reaction or a deactivation, a chain is broken (Staudinger). The presence of an unsaturated group has been considered as the activating factor in polymerization, the degree of which depends on external conditions of the reaction, such as temperature and catalyst, as well as on the type of the substituent groups.<sup>76</sup> The unsaturated groups are found more or less abundantly in hydrocarbons, aldehydes, alcohols, acids, esters, ethers, lactones, nitriles, isonitriles, salts of unsaturated organic acids, etc.

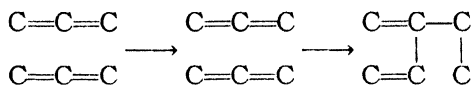
It has been postulated<sup>26</sup> that the essential part in the activation of molecules in all transformations of unsaturated compounds consists in breaking the double bond and converting the tetravalent carbon atom into the trivalent carbon atom, whereby it is brought into the unsaturated state and chemical energy to complete the process is supplied. The activation energy is equal to the energy of rupture of one double bond in the absence of a chain reaction. Active molecules react with normal molecules, but not with one another, in order to form polymerization products. Thus, Gapon assumes in the formation of dimers, as well as of polymers, that the first stage of polymerization consists in connecting two molecules at their ends.



Since neighboring valences are used for the formation of the double bond, the closing of the system consisting of 6- and 8-membered rings and combining of the links into a ring may proceed in three directions:

- (1)  $\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}$  (structure of the dimer form)  
 (2)  $\text{C}-\text{C}=\text{C}-\text{C}-\text{C}-\text{C}=\text{C}-\text{C}$   
 (3)  $\left[ -\text{C}-\text{C}=\text{C}-\text{C}-\text{C}-\text{C}=\text{C}-\text{C}-\text{C}- \right]_x$  (structure of the polymer form)

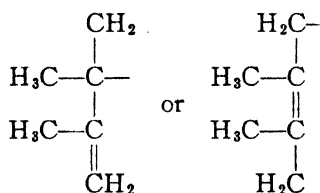
The scheme of the polymerization of allene hydrocarbons, in which two molecules combine at the middle atoms, has been given by Lebedew<sup>55</sup> and Lebedew and Meregowskii:<sup>55, 56</sup>



Applying the assumption that polymerization is preceded by the activation of molecules, these schemes should be changed in accordance with

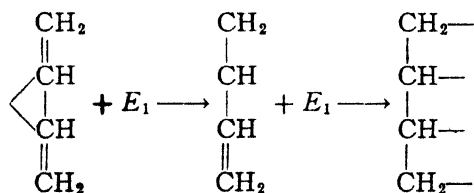
Thiele's<sup>98</sup> partial valence theory to:  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ .

Gapon has listed the rules for the polymerization of the divinyl and allene series. The number of primary products yielded in the polymerization of hydrocarbons of these series and their symmetrically substituted derivatives has been postulated to be equal to the number of active forms produced in the activation of the monomer. For example, according to Gapon, by the activation of a molecule of 2,3-dimethylbutadiene either of two active forms may originate:



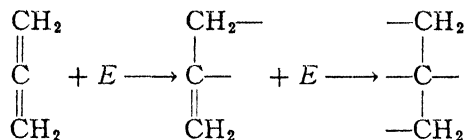
and a combination of these leads to the formation of the dimer, while combinations of the second give rise to the polymer.

The activation of the divinyl molecule was stated by Gapon to proceed according to the following scheme:



where  $E_1$  is the energy of activation equal to the energy of rupture of the double bond  $\text{C}=\text{C} \longrightarrow \text{C}-\text{C}$ . Activation of the allene molecule has been given as follows:





The scheme of activation of the isoprene molecule reveals that three active forms are obtained.

In connection with the polymerization of monoolefins, it has been emphasized by Vaughan<sup>102, 103</sup> that simple dimer formation is not only the first step in the reaction, but also the most important one.

Lebedew has shown that in the polymerization of hydrocarbons of the divinyl series the relative amounts of the dimer and polymer are constant during the course of the reaction, provided the temperature remains constant. Therefrom he deduced that polymerization proceeds in two different directions: (1) from monomer to dimer, and (2) from monomer to polymer. With respect to the divinyl series he has pointed out: (1) the displacement of the substituent from the middle atom of a conjugated system decreases the velocity of polymerization; (2) the formation of a ring from a chain in a conjugated system increases the velocity of polymerization; and finally (3) in a homologous series an increase of the mass of a substituent at the middle (or extreme) atoms of a conjugated system increases (or lowers) the velocity of polymerization at corresponding temperatures. From results obtained by Lebedew for four allene derivatives, he concludes that: (1) the velocity of polymerization of isomeric hydrocarbons of the allene series does not depend on the positions of the substituent groups, and (2) in a homologous series of allene hydrocarbons increase in the mass of the substituent results in increased velocity of polymerization at the corresponding temperature.

Gapon<sup>27</sup> has stated that the process of polymerization of hydrocarbons of the allene series differs from that of the hydrocarbons of the divinyl series in the fact that in the latter case monomeride molecules combine with one another and with the polymeride, whereas in the allene series both these processes and that of combination between polymeride molecules take place. The number of primary polymerides of hydrocarbons of the divinyl series, as well as sulfur-substituted allene hydrocarbons, is equal to the number of types of active molecules; but in the case of allenes it is greater. In general, the velocity of polymerization of sulfur-substituted hydrocarbons is greater, and diminishes with increase in the homologous series. The introduction of a methyl group into the divinyl hydrocarbon reduces the velocity of polymerization by 80 per cent, while introduction of the methyl group into the allene hydrocarbon decreases the polymerization velocity only about 33 per cent. In addition, it has been shown that retardation of the velocity due to the introduction of a substituent is greater when the terminal atom, rather than the central atoms, of the chain is affected.

The  $\text{C}_8\text{H}_8$  hydrocarbon of the divinyl series also shows a higher velocity of polymerization than the structural isomerides of the allene series. The reverse holds true for the  $\text{C}_6\text{H}_{10}$  hydrocarbon of these two series. Many

substances, though present in the same unsaturated state, may possess different polymerization ability and polymerization velocity. The ability of a chemical compound to polymerize depends not only on the structure of the molecule, but on external influences, such as catalysts, regulators, buffer substances, etc. The polymerization velocity is affected chiefly by heat, pressure, light and catalysts. In some unsaturated compounds polymerization proceeds spontaneously in the cold, in others first by heating (formaldehyde, styrene, acrylic ester). Light favors, for instance, the polymerization of vinyl acetic acid, vinyl chloride and vinyl bromide.

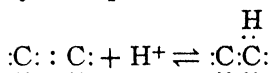
Many compounds may be converted into polymer compounds only through catalysts. Common catalysts of polymerization processes are: peroxides, metal halides and metalloids with a tendency to change into complex compounds; likewise acids, bases, metals and active earths. Polymerization may be effected by small additions of a polymer to the monomer, *i.e.*, germ catalysis.<sup>65</sup> A different course of polymerization due to the type of catalyst used, has been recognized<sup>98</sup> in the case of styrene. This may be converted by denite catalysts into distyrene, while in spontaneous polymerization or by means of other catalysts high molecular weight polystyrenes are formed. The same is true in the case of butadiene polymerization. Unsaturated compounds which polymerize only over catalysts are, for example, isobutylene, anethol, indene, ethylene oxide, propenyl, benzene, etc.

Ziegler and Bähr<sup>110</sup> proposed the following mechanism for polymerization by alkali metals. The possibility of addition depends on the presence of conjugated double linkages or a double linkage adjacent to the benzene nucleus. Polymerization of an unsaturated organic compound, such as butadiene, by an alkali metal may be explained by assuming that the primary compound,  $\text{CH}_2\text{RCH}(\text{R})\text{CH}=\text{CH}_2$ , is itself an alkali metal compound and hence can react further with another molecule of butadiene, giving as the product:  $\text{CH}_2\text{RCH}(\text{CH}=\text{CH}_2) \cdot \text{CH}_2\text{CH}(\text{R})\text{CH}=\text{CH}_2$ . The process may continue until it is stopped by some external agent, a change in the direction of the process, or by increase in the size of the molecule, which may induce considerable sluggishness in the reaction.

With reference to polymerization of vinyl acetic acid, it has been assumed<sup>91</sup> that many individual molecules unite by normal covalences to form a long chain. A chain mechanism has been suggested for the interpretation of the polymerization of aliphatic aldehydes and isoprene under high pressure, using peroxides as catalysts. The possibility that the polymerization of unsaturated compounds is related to the tendency of their molecules to arrange themselves so that they have a minimum electric moment, so that union of chemical linkages may take place, has been advanced by Oda.<sup>67</sup>

According to Whitmore<sup>106</sup> the polymerization of olefins can best be explained by assuming a positive complex formation resulting from a proton addition to the double bond, which in its turn adds to the double bond of another olefin molecule forming a still larger complex. The latter can lose a proton and become a dimer, or previously rearrange and then lose a

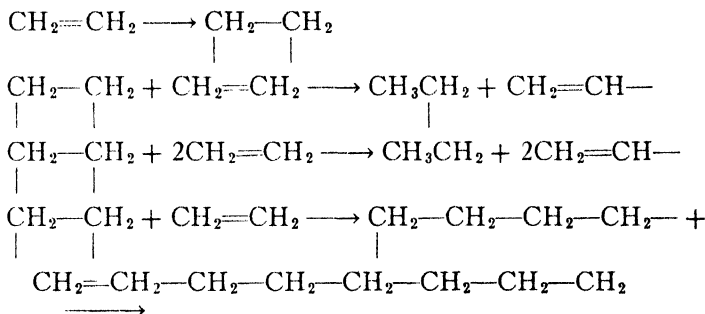
proton, or polymerize still further. In each step of polymerization the existing state is given<sup>107</sup> by the equation:



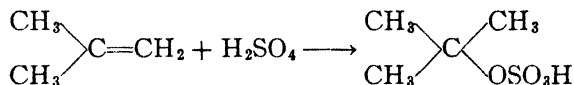
Polymerization has been interpreted also as a combination of labile molecules such as those containing  $\text{=CH}_2\text{—CH=CH}_2$  and  $\text{=C=CH}_2$ .

Taylor and Jones<sup>97</sup> experiment on the decomposition of tetraethyl lead in the presence of ethylene, which leads to its polymerization, has been considered as a proof of the action of the ethyl radicals in the polymerization process. The polymerization of paraffin oil, oleic acid and olive oil by atomic hydrogen has been interpreted<sup>49</sup> in the sense that hydrogen atoms split the large molecules to form radicals, which then combine. A free radical theory of polymerization, for example, those of the type  $\text{CH}_2\text{—CH}_2$

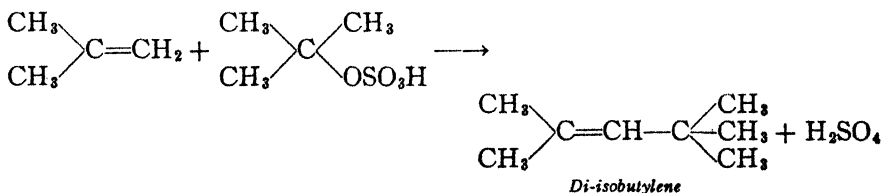
has been favored by Hurd.<sup>33</sup> According to this viewpoint polymerization of ethylene proceeds as follows:



Rice<sup>73</sup> postulates the scission of the C—C bonds to form free radicals of the alkyl type in the case of thermal reactions of olefinic hydrocarbons. Polymerization of olefins in the presence of sulfuric acid has been considered to proceed through the intermediate formation of the alkyl sulfonic acid according to the equation given by Kondakow<sup>43</sup>

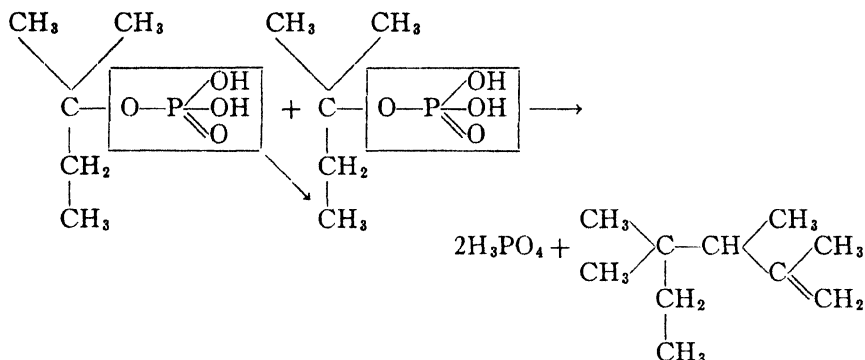


which then reacts with another molecule of the olefin:

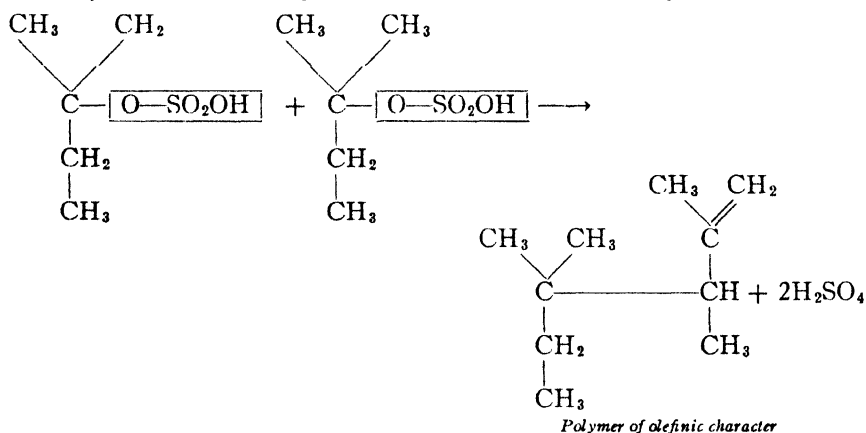


Polymerization in the presence of anhydrous metallic salts such as aluminum chloride has been assumed to involve the intermediary formation of organo-metallic complexes.

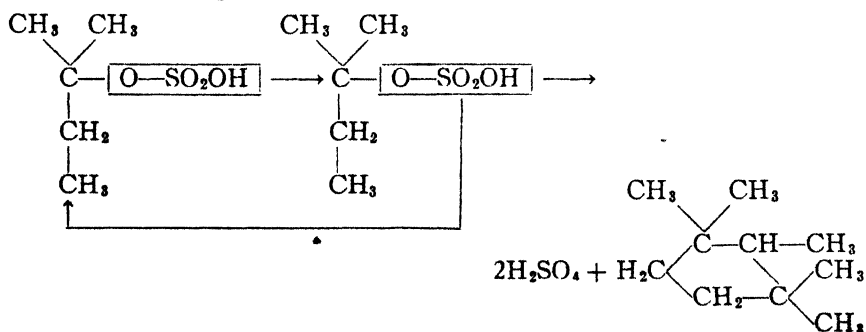
Ipatieff<sup>35</sup> proposed the following scheme for the polymerization of amylene under the influence of  $\text{H}_3\text{PO}_4$  as catalyst.



Formation of the unstable amyl ester of phosphoric acid is the intermediate stage of polymerization, which then proceeds by withdrawing the elements of phosphoric acid from the two molecules of ester. The scheme in the polymerization of amylene with sulfuric acid as catalyst is similar.



Likewise a naphthene may be formed as the polymer product according to the following equation:



In interpreting the mechanism by which aliphatic and aromatic ethylene derivatives polymerize with acids, some metals or metalloid halides, Schmitz-Dumont, Thömke and Diebold<sup>75</sup> considered the relationship between the polymerization ability and the constants of monomers. Assuming with Michael<sup>64</sup> that the polymerization ability of an ethylene derivative is caused by a polar opposition of both ethylene carbon atoms, and that asymmetrically substituted ethylenes show a pronounced inclination to polymerize, the polymerization ability of the derivative of the asymmetrical diphenyl ethylene in acetic acid with  $\text{H}_2\text{SO}_4$  catalyst has been studied. The dimeric product formed thereby is  $(\text{C}_6\text{H}_5)_2\text{C}(\text{CH}_3) - \text{CH}=\text{C}(\text{C}_6\text{H}_5)_2$ . The polarity of the ethylene binding is altered by the introduction of positive or negative acting substitutes into the phenyl groups. A negatively acting group such as Br causes the polarity of the ethylene binding to weaken;  $\beta$ -bromdiphenylethylene does not polymerize under the given conditions. On the other hand, however, a too strong positive action, as in the case of *p-p'*-dimethoxydiphenylethylene, decreases the polymerization ability. On the contrary, ethylenes rendered less strongly positive may be readily polymerized as in the case of tolylphenylethylene, ditolyethylenes and  $\beta$ -methoxydiphenylethylene. By introducing Br atoms in the *ortho* position to the methoxy-groups and so weakening the too strong positive action in *p, p'*-dimethoxydiphenylethylene, a product with great tendency to polymerize has been obtained. Under the influence of concentrated  $\text{H}_2\text{SO}_4$  the dimers undergo depolymerization. The dimer diarylethylene depolymerizes with four mols  $\text{Br}_2$  in  $\text{CHCl}_3$ , and the monomeric diaryldibromomethylene is formed with splitting off of  $\text{HBr}$ . Under the action of only one molecule of  $\text{Br}_2$  dimeric dehydrogenation products free from bromine are formed.

In certain polymerization processes, for example, that of unsaturated hydrocarbons under the influence of  $\text{AlCl}_3$ , three groups of hydrocarbons result, namely, saturated hydrocarbons, unsaturated polymer products and aromatics. If the relation between unsaturated and aromatic hydrocarbons originating from the initial unsaturated hydrocarbons through reactions in the presence of aluminum chloride is genetic, it is to be expected that the end product would contain less unsaturated hydrocarbons the higher the content of aromatics, and *vice versa*. This has been postulated by Nametkin and Rudenko<sup>66</sup> and proved experimentally in the case of polymerization of cyclohexene with  $\text{AlCl}_3$  at  $50^\circ$ . The reaction actually taking place by the action of  $\text{AlCl}_3$  as catalyst is described as follows: a part of the polymers is dehydropolymerized by the formation either of highly unsaturated polymers, which remain in a complex compound formed with  $\text{AlCl}_3$ , or of aromatics; another part of the polymers is hydrogenated by formation of hydropolymers, and therein the splitting action of  $\text{AlCl}_3$  is also involved.

Many investigators are of the opinion that the most plausible mechanism by which polymerization is set forth is a kind of chain formation. Dostal and Mark<sup>18</sup> assume that chains lead to the formation of macro-

molecules. The first step in the process is recognized as a germ formation; this is followed by a growth process. The germ formation velocity is considered to be a reaction of a monomolecular order (through light adsorption or catalysis) or bimolecular (in the case of normal thermal polymerization). With definite assumptions for the germ formation and the velocity of growth, the distribution of the substance polymerized in various degrees of polymerization in various stages of the process (time =  $\infty$ ) has been calculated. The degree of polymerization has been found to be most pronounced at the end. The distribution for monomolecular germ formation is approximately:

$$1.3 \sqrt{\frac{\text{Reaction constant of chain growth}}{\text{Reaction constant of germ formation}}}$$

The distribution for bimolecular germ formation is:

$$1.4 \sqrt{\frac{\text{Reaction constant of chain growth}}{\text{Reaction constant of germ formation}}}$$

Dostal and Mark support the growing radical type of chain, and consider the nuclei-forming process to be either mono- or bimolecular. Breitenbach and Forde,<sup>7</sup> from the two possible mechanisms of polymerization involving either autocatalytic or chain reactions, chose the latter as the more plausible for the interpretation of the formation of high-polymer compounds from molecules of the same kind.

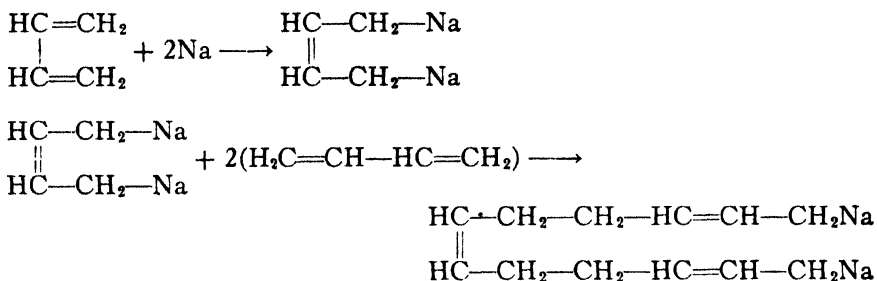
The beginning, growth, breaking off and branching of chains are in general partial reactions of the kinetics actually measured in the process.

The induction period which corresponds to the average duration of the chain growth has been experimentally proved. It depends on the special characteristics of the reaction. Polymerization reactions may be readily studied with styrol, which polymerizes even at low temperatures. The single partial processes proceed predominantly in the homogeneous phase. The polymerization velocity and average chain length of the polymerizate are found to be independent of the surface of the walls of the container as well as of its pretreatment. The polymerization is stated to proceed more slowly in air than in nitrogen or in a high vacuum. The removal of all gas traces has no influence upon the velocity of polymerization. It has been stated by Dostal and Mark<sup>19</sup> that the induction period in a polymerization reaction is based on the presence of atmospheric oxygen.

Meyer and Mark<sup>68</sup> agree with Staudinger's viewpoint that highly polymerized natural substances consist of molecules forming long chains which are held together by normal chemical main valences. In solution the arrangement of molecules is very complex, and in general neither homogeneous micelles nor isolated main valence chains are present. Due to the marked action of the solvent the dissolved particles differ from the micelles in the solid.

A chain-like mechanism for catalytic polymerization of butadiene by sodium has been proposed by Abkin and Medwedev.<sup>1</sup> The induction period

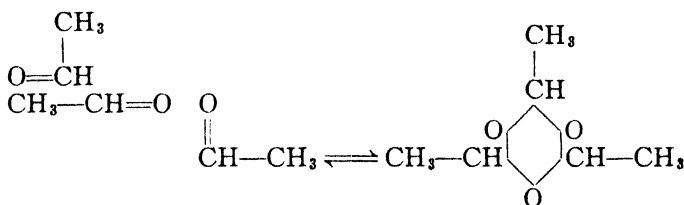
in the reaction has been thought to correspond to the time required for butadiene to combine with the catalyst according to the scheme:



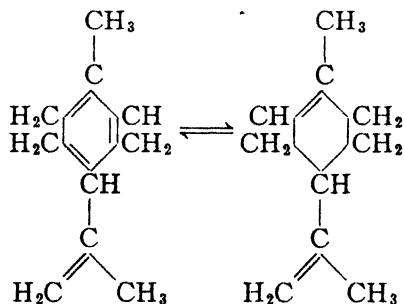
### Depolymerization

Depolymerization is the reverse process of polymerization. The following reactions are examples in which the conversion of the monomer form into the polymer form is reversed.

3 molecules acetaldehyde  $\rightleftharpoons$  1 molecule paraldehyde



2 molecules isoprene  $\longrightarrow$  1 molecule dipentene



Processes of depolymerization represent one type of disaggregation phenomena and are usually accompanied by absorption of heat. Depolymerization, in contrast to polymerization, involves the resolving of atomic bonds of organic molecules. The readiness with which definite compounds are affected by a chemical attack depends, primarily, on the kind of atoms linked together. In many cases depolymerization is concerned with the loosening of the C—H, C—O, C—N and especially C—C bonds. The depolymerization of olefins or polystyrols involves chiefly the loosening of these stable bonds. Sometimes the O—H and N—H bonds are broken and,

in these instances, the change is easily effected. It has been ascertained that the process: monomer molecules  $\rightleftharpoons$  polymer molecules is more likely to occur with molecules having a thread-like structure than with those of the so-called three-dimensional or spherical type. In the depolymerization of three-dimensional macro-molecules, not only the monomers and dimers but also considerable amounts of other, low molecular weight polymers are formed, depending on the type of molecule and the conditions of the reaction. Depolymerization of dicyclopentadiene in the gaseous phase shows that the reaction proceeds monomolecularly, with a velocity expressed by the equation  $K = 1.0 \cdot 10^{13} e^{-33,700/RT}$  sec.<sup>-1</sup>.

In discussing the kinetics of the polymerization of styrene, vinyl acetylene, chloroprene, vinyl acetic acid and allene cyclopentadiene in the gaseous phase, Harkness, Kistiakowsky and Mears<sup>27b</sup> concluded that these reactions involved the free radical mechanism. In the case of 1,3-butadiene,

the radical has a structure  $\text{C}=\text{C}-\overset{|}{\text{C}}-\text{C}-\overset{|}{\text{C}}-\text{C}=\text{C}$  which is supposed to be stabilized by a resonance between four possible electronic structures.

By the depolymerization of Resite in a hydrogen atmosphere, Waterman<sup>105</sup> obtained from the three-dimensional macro-molecules phenol, cresol, benzene and toluene as well as a considerable amount of high-boiling polynuclear aromatic compounds of the Resitole type. The depolymerization of polystyrene or polyacrylic acid ester results in the almost exclusive production of monomeric compounds.

With respect to the stability of high molecular weight organic compounds a marked difference has been observed depending upon the shape of the molecules constituting them. While thread-like molecules depolymerize more readily the longer their particle length, the three-dimensional molecules increase in stability with roundness in shape.

The depolymerization ability may be judged to a certain extent from the way in which a certain polymer has been formed. For instance, depolymerization should be expected if the polymerization and depolymerization are part of one and the same reversible process. The process of depolymerization of polymer forms of isobutylene may be greatly facilitated by the correct choice of a catalyst affecting it. In the latter case depolymerization is difficult without a catalyst, but proceeds with ease in the presence of fluoridine. There are two methods for depolymerization of isobutylene: (1) distillation over a catalyst, and (2) passing it through a tube with heated fluoridine.

Depolymerization of all polymers is accompanied by the formation of a dimer and the liberation of gaseous hydrocarbons consisting almost exclusively of unsaturated members. The pentamer is synthesized from the dimer and trimer:  $(\text{C}_4\text{H}_8)_2 + (\text{C}_4\text{H}_8)_3 \rightleftharpoons (\text{C}_4\text{H}_8)_5$ . The trimer polymerizes alone and, in a mixture with the readily polymerized dimer, is able to form the pentamer. This reaction is reversible. The doubling of the dimer is also a reversible process:  $(\text{C}_4\text{H}_8)_2 + (\text{C}_4\text{H}_8)_2 \rightleftharpoons (\text{C}_4\text{H}_8)_4$ . This is not the case when a dimer combines with the monomer:  $(\text{C}_4\text{H}_8)_2 + \text{C}_4\text{H}_8 \longrightarrow (\text{C}_4\text{H}_8)_3$ . The dimer is the less stable polymer of isobutylene and dissociates into two molecules of isobutylene:  $\text{C}_4\text{H}_8 + \text{C}_4\text{H}_8 \rightleftharpoons (\text{C}_4\text{H}_8)_2$ .



Dissociation and synthesis of polymers, the dimer participating chiefly, occurs in the presence of a small amount of the monomer, isobutylene.<sup>64</sup> Carothers, Dorough and van Natta,<sup>11</sup> discussing examples of reversible polymerization of six-membered cyclic esters, conclude that reversible polymerization is generally characteristic of six-membered cyclic esters; ester-rings containing five, or more than six, atoms are not polymerized by heat. The tendency of six-membered cyclic esters to polymerize reversibly is stated to be related to their susceptibility toward hydrolysis. Both tendencies are diminished by the presence of substituent groups. The polymerides formed are linear poly-esters, and in certain cases the chains are open and are terminated by the OH and COOH groups. Both polymerization and depolymerization are essentially processes of ester interchange. The peculiar position occupied in this sense by the six-membered cyclic esters has been explained by stereochemical considerations based on the Sachs-Mohr theory.

Among facts observed with regard to depolymerization is that the relative length of molecule chains decreases with increase in depolymerization and that high temperatures decrease both the viscosity and the degree of polymerization.<sup>20</sup>

### Degree of Polymerization

The extent of polymerization varies within broad limits. In the case of many substances the dimers, trimers and tetramers or pentamers, as well as low polymers (hemi-colloids of molecular weight 4,000–10,000), medium polymers (meso-colloids of molecular weight 10,000–70,000), and high polymers (eucolloids of molecular weight 70,000–1,000,000) are known. Only in rare cases does polymerization lead to the formation of products of equal molecular weight. Ordinarily, high-polymer products contain large complexes admixed with low polymers. The state of a resin even in the early stages of polymerization may be shown to be a mixture of substances.

The transition from an unsaturated monomer substance into a polymer may proceed in a different manner, the end-product depending on the type of the reaction. In many cases it is difficult to differentiate between the reactions involved. Of great influence upon the course of polymerization is the manner in which polymerization occurs. A product polymerized in a solution or in an emulsion is very different from the pure polymerizate and usually shows a different degree of polymerization. The course of polymerization and the physical properties of the products are influenced by such factors as the initial concentration of the solution and the continuous addition of the monomer product. In fact, the influence of the solvent, as in other chemical reactions, plays an important role.<sup>17, 52</sup> For instance, in the polymerization of butadiene by lithium in benzene, one or two additions occur, while in ether a stronger polymerization takes place because one to four additions were proved.<sup>109</sup> In estimating the degree of polymerization, it is essential to know that a polymerization process may be retarded by certain substances, or even completely stopped. In case it is

necessary to keep polymerizable compounds in storage or to distill them in a monomer state, anticalysts or stabilizers have to be added.

Little is known of the action of such substances as, for example, mono- or polyvalent phenols, iodine, sulfur metal or metal salts with respect to many polymerizable compounds. For instance, it has been established that styrol may be kept in a monomer state by additions of sulfur or hydroquinone. However it is believed that the influence exerted is due to hindering of the auto-oxidation and the formation of peroxydic intermediate compounds which would produce the reaction germs for the polymerization chain.

To estimate the degree of polymerization a formula was proposed by Konrad, Bächle and Signer:<sup>45</sup>  $p = n/(n-m)$ , where  $p(=x+2)$  is the degree of polymerization produced by the action of  $m$  molecules of water upon  $n$  molecules of an *ortho* ester. Studying the viscosity of polymerized methyl styrene in benzene solution Staudinger and Brensch<sup>88</sup> found that it increases more rapidly than required by the proportionality of molecular weight. This was interpreted as evidence of the fact that in case of polymeric homologous compounds the degree of polymerization may be determined by comparing the viscosities of equally concentrated solutions with respect to the unit molecule. Density and refractive indices were found to increase with the degree of polymerization. It has been stated also that the dimeride and tetrameride were found to be crystalline, whereas other polymethyl styrenes were amorphous. The pentameride polymerized to the octameride of  $\alpha$ -methyl styrene shows an increase in liquefaction temperature with degree of polymerization, thus being a criterion of the latter.

Colloidal properties of the polymerides not shown by simpler members of the styrene series appear only when their degree of polymerization is high. The rate of polymerization appears to be closely related to the degree of polymerization.

Starkweather and Taylor,<sup>78</sup> investigating the mechanism by which a monomer is converted into a polymer in the polymerization of vinyl acetate, determined the velocity of polymerization by observing the contraction of volume. They found a linear relationship between the percentage of the contracted volume of the initial monomer and the degree of polymerization. The measurements were carried out by evaporating the mixture of the monomer and polymer until a constant weight was obtained (polymers are not volatile). The reaction is monomolecular and occurs by union of chains. It is believed that in order to obtain products of satisfactory elastic properties an optimum degree of polymerization must be attained. Thus it is of great importance to know how far polymerization proceeds in order to judge the state of the substance (whether molecular or colloidal) as well as the changes of properties closely related to it. When the chain length increases, the number of particles decreases. When the average degree of polymerization is 1000, the sphere of action of particles is estimated to be  $9 \cdot 10^{23}$ ; for a degree of 100 it is  $9 \cdot 10^{22}$  and  $9 \cdot 10^{21}$  for a value of 10. Only in case of extreme dilution does the solution contain macro-molecules. As the solution becomes more concentrated the macro-molecules, because

of their length, are limited in their movement and resist one another; this fact is considered an explanation for the decided increase in viscosity with concentration, previously explained as a solvation effect.

The differences in the properties of polymerized products were related by Staudinger to the degree of polymerization and the end-group in the chain of molecules, which determine the reactions of the thread molecules. The formation of products of various degrees of polymerization may be understood from the fact that ring closure is produced more rapidly by catalysts or by heating than is polymerization in the cold.<sup>74</sup> On the other hand, the extent of the dependence of the properties of the polymerized products on the degree of polymerization has been shown by Katz<sup>41</sup> and Wo. Ostwald,<sup>71</sup> in the explanation they give to the fact that in latex and crude caoutchouc the internal portion of the particles is less solid than their walls. The difference has been attributed to the different degrees of polymerization of the hydrocarbons. The greater the polymerization of the substance, the stronger the solid properties and the weaker the liquid properties. On the contrary, the less polymerized, the weaker the solid properties and the stronger the liquid properties.

Kirchhoff<sup>72</sup> pointed out that the degree of polymerization determines also the amount of the polymer. He studied the cyclization of hydrocarbons of caoutchouc in the presence of  $\text{AlCl}_3$  in  $\text{CCl}_4$  activated by  $\text{HCl}$  (separated from benzyl chloride and effective in the condensation process), the amount of polymer obtained being regarded by him as a function of the concentration of caoutchouc as well as of its degree of polymerization.

Minute traces of certain reagents such as, for instance, metallic sodium, are sometimes sufficient to bring about polymerization of large masses in the conversion of isoprene into synthetic rubber. Because of its colloidal nature, its molecules being formed by the union of fundamental molecules, isoprene is in a state of continuous flux, passing from one degree of polymerization to another, so that the internal equilibrium undergoes continuous changes. The presence of  $\text{CO}_2$  or  $\text{O}_2$  in the distillation flask, when polymerizing isoprene (myrcene, limonene, pinene, etc.) affected the rate of polymerization. The polymerization occurred more rapidly in the presence of  $\text{O}_2$  than in the presence of  $\text{CO}_2$ , but the absolute differences in the rates of polymerization were found to be small.<sup>90</sup>

It is known that the tendency of olefins to polymerize increases with increasing molecular weight from ethylene upward, but reaches a maximum with the hexenes and heptenes. The proximity of other double bonds as, for instance, in the case of conjugated diolefins, increases the ability to polymerize. Negative groups such as phenyl (styrene), halogens (vinyl halides) and acidic groups (vinyl esters) act in the same sense. It has been ascertained also that polymerization may proceed more rapidly in the presence of air or oxygen; this is the case in the drying of vegetable oils or in the formation of gums in unsaturated gasolines.

### Polymerization Products

Although there are points of similarity between low and high molecular weight organic compounds, there are important differences in their physical

properties and sometimes in their chemical structure. These differences have been summarized in Table 2.

Table 2.

Property	Low Molecular <10,000	High Molecular >10,000
Molecular weight.		
Number of atoms in molecule.	<1000	>1000
Structure.	Unit molecules.	Unified polymer molecules.
Crystal structure.	Molecular lattice.	Macro-Molecular lattice.
Solution.	Molecular solution (monodispersed system).	Macro-molecular solution (colloidal solution).
Method of preparation.	Synthesis.	Polymerization, polycondensation.

About 300,000 low molecular weight organic compounds are known today, the majority of which have a molecular weight below 1000, while a few have a molecular weight up to and above 4000. The number of atoms forming such molecules is comparatively small. The molecules of high molecular weight compounds are composed not of a few hundred, but of one and even ten million atoms. These high molecular weight substances require different conditions for their preparation and special methods for determination of their composition. Their chemical and physical behavior is also specific.

A new method has been devised for determining the molecular weights of high molecular weight compounds. By considering the colloidal properties of these substances or their derivatives in a dissolved state, viscosity measurements were found to be the most appropriate for the determination of the molecular weights of many natural and synthetic high molecular weight compounds. By chemical determination of the end-groups of high polymer molecules in poly-oxymethylene, it was found that these molecules are built in the same manner as those in low molecular weight compounds, the chain or thread-like shape predominating. This finding was applied to many synthetic high-polymer substances and acknowledged as a basis for determining the structure of natural high molecular weight substances. By cryoscopic and osmotic molecular weight determinations, as well as by hydrogenation and the formation of derivatives, or reprecipitation of high molecular weight molecules, it has been concluded that polymer particles are not small micelles, but molecules in the sense of classical organic chemistry. Further, the investigation of polymer compounds must include: (1) unit (monomer molecules) building up the polymer; (2) type of linkage involved; and (3) size, as well as form of particles.

X-ray measurements assist greatly in the study of the original units constituting the polymer. Physical properties, such as viscosity, elasticity, and solidity, and chemical properties, such as resistance to water and other reagents, are determined both by the nature of the fundamental (base) molecules and the size and configuration of the polymer particles. Considering both natural and synthetic polymer products, the question arises whether the growth of the molecule to form a polymer involves a chemical

reaction or a physical process. Investigations in colloidal chemistry led to the conclusion that the classical conception of molecules does not apply to high molecular weight substances. It has often been thought that these polymer compounds are not built up in the same way as low molecular weight compounds, but that through a physical process called aggregation the particle increases in size, forming a micelle. Numerous works of Staudinger prove, however, that the majority of polymer compounds should be considered as particles in which certain atoms are linked through main valences, such as is the case with low molecular weight compounds like the paraffin hydrocarbons.

The products obtained by chain polymerization are distinguished from those obtained by condensation-polymerization by the size of their molecules. In poly-condensation or condensation-polymerization, no such large molecules are formed as by chain polymerization, because the reaction ability decreases with an increase in the molecule, thus indicating that the condensation processes slow down. Staudinger has stated that polymers obtained through condensation-polymerization, insofar as they are soluble, have a hemi-colloidal character. On the contrary, products originating at sufficiently low temperatures by chain polymerization are extremely high in molecular weight, differ greatly in molecular size and, if soluble, form solutions of a eucolloidal character.

The relationship between viscosity of a high molecular weight solution and the molecular weight, or the chain length, first emphasized by Biltz,<sup>6</sup> is of great importance. The viscosity of equally concentrated starch solutions has been found to increase with an increase in the particle size. Equally concentrated solutions of disintegrated cellulose had lower viscosities than the starting products.<sup>70</sup> The same relationship has been found<sup>2, 21, 86</sup> for natural and synthetic high polymers between viscosity of equally concentrated solutions and the degree of disintegration or polymerization.

Differences established in the chain length of polymers may account for the specificity found in the properties of high molecular weight colloids and the kind of polymerization which led to their formation. The difference in the kind of polymerization in the case of natural products (natural rubber) and synthetic rubber may be the reason for striking variability in properties as well as in behavior. Quite often polymerization does not result in the building up of a definite high-polymer substance, but rather forms a mixture of polymerization products. Polystyrene, for instance,<sup>82</sup> consists of many polymers having the same principal structure, but distinguished by the length of the chain. Staudinger refers to these polymers as polymer homologs.<sup>84</sup> It has been found that the tendency of  $\alpha$ -methylstyrene to polymerize is much less than that of styrene; therefore shorter chains are produced and ring closure takes place when only a few molecules have become attached to one another. Thus a polymeric homologous series of polymethylstyrenes results, extending from dimeric to octameric members. The presence of rings is established by the saturated character of products obtained and the absence of other residues as terminal groups.<sup>88</sup> The polystyrenes and polyindenes, similar in molecular structure, are formed like methylstyrenes

from long chains, the terminal valences of which become saturated by forming rings.<sup>89</sup>

Carothers and Arvin<sup>10</sup> recognize two types of linear polymerides ( $R$ )<sub>n</sub>: (1) addition polymerides (caoutchouc, polystyrene, polyoxymethylenes) in which the polymeride has the same composition as the monomeric compound, and (2) condensation polymerides (cellulose, hexaethylene, glycol) in which the monomeric compound differs from the structural unit ( $R$ ) by  $H_2O$ ,  $NH_3$ ,  $HCl$ , etc. On the other hand, high molecular weight substances encountered in nature have been classified<sup>24</sup> into three groups: (1) homopolar molecule colloids, to which belong hydrocarbons like polystyrol and polyprène, and also caoutchouc, gutta percha and balata; (2) macro-molecules with a dipole character, entering into coördinative combinations and called coördinative molecule colloids, such as polyvinyl alcohol, polysaccharides, polyacrylic acids (in non-dissociated state) and albumin (in non-dissociated state); and (3) heteropolar molecule colloids, among which are found polyacrylic acid in the ionized state, salts of polyacrylic acid, caoutchouc, phosphonium salts and ionized albumin.

The relationship between the structure of polymers and their physical properties should not be overlooked. It has been established<sup>40</sup> that with an increase in intermolecular compounds of single molecule chains the solubility, especially in aromatic solvents, decreases, while the viscosity and gelatinizing ability increase. The distance between the reactive groups in the molecule has an important effect in determining the characteristics of polymers; for example, an increase in distance will lower the solidity of the product. The influence of polymerization on the magnetic susceptibility has been investigated by Bhatnagar, Nervgi and Mathur.<sup>4</sup> Using the magnetic interference balance by Bhatnagar, Mathur tested anthracene, dianthracene, acetone, diacetone alcohol, benzaldehyde, benzyl benzoate, benzoin, furfural, furoin, acetyl cyanide, and diacetyl cyanide. It was proved that the true, as well as the condensed polymers, become more diamagnetic on polymerization.

Farquharson and Ady<sup>28a</sup> postulated that because of the disappearance of double bonds by polymerization the diamagnetism increases. However, 2,4-dimethylbutadiene gave a decrease in diamagnetism, after which an increase was observed. This is explained by the formation of free radicals first, and their concentration is about 0.10 mol per cent. On the contrary, if a catalyst such as benzoyl peroxide is added, the preliminary decrease in diamagnetism is eliminated and the diamagnetism increases from the beginning. The concentration of the catalyst required for a smooth course of the curve is about 0.17–0.34 mol per cent, *e.g.*, about the order of magnitude equal to the content of free radicals formed in a process without a catalyst.

### Industrial Polymerization Processes

Catalytic polymerization in industrial organic chemistry finds its principal application in the production of synthetic rubber, resins, lubricating oils and gasoline. With the success in the production of rubber-like synthetic products due to catalytic polymerization of diolefins, such as butadiene and its simple homologs isoprene, piperylene and 2, 3-dimethyl-

1,3-butadiene, etc., are associated the names of the following early investigators: Williams,<sup>108</sup> Tilden,<sup>100</sup> Kondakow,<sup>44</sup> Ostromislensky and Koschelev,<sup>68</sup> Mathews and Strange<sup>69</sup> and Harries.<sup>28</sup>

In the modern synthetic rubber processes isoprene is synthesized from acetylene derived from coal or from gaseous by-products of the petroleum industry. The polymerization of isoprene is conducted in a colloidal solution (for example, egg albumen, sodium oleate, or Turkey red oil) and with careful control of the acidity of the reacting mixture. The product is rolled into sheets with sulfur and vulcanized in the ordinary way. Strength and elasticity of the polymer are the essential characteristics to be considered.

The catalytic polymerization of coumarone and indene or their homologs obtained from heavy benzene or solvent naphtha fractions of coal-tar distillation (usually in the presence of  $\text{H}_2\text{SO}_4$  catalyst) leads to the formation of the corresponding resins. This process was discovered by Kraemer and Spilker.<sup>46</sup> Resins have been prepared also from styrene, which is a product of coal carbonization or is obtained by pyrolysis of ethyl benzene. Metallic sodium or potassium, anhydrous metallic halides and aryl diazonium fluoroborates have been recommended as catalysts for technical polymerization.<sup>9</sup> Among other unsaturated substances suited for the production of resins are vinyl esters (Ba peroxide catalyst). Thomas and Carmody<sup>99</sup> state that the highly unsaturated, less stable diolefins yield resinous polymers.

The polymerizing and condensing action of  $\text{AlCl}_3$  has been utilized in the production of synthetic lubricating oils. Since Ipatieff and Rutala<sup>38</sup> showed that polymerization of ethylene with  $\text{AlCl}_3$  catalyst at  $0^\circ$  under pressure leads to the formation of hydrocarbons of a very high molecular weight, investigators studied other catalysts such as anhydrous ferric and zinc chlorides and found that they act in a similar manner, but require the use of higher temperatures. Viscous oils obtained by polymerization of ethylene with  $\text{AlCl}_3$  as catalyst and suitable as lubricants were described by Stanley, Nash and Bowen.<sup>77</sup>

The properties of oils produced by polymerization depend first of all upon the type of olefinic material used for the process. Among the open chain olefins, the homologs of ethylene polymerize more readily than ethylene itself. The viscosity indices improve with increasing chain length of the initial olefin. For instance, polymerized oils obtained from cetene with 16 carbon atoms in the chain had viscosity indices as high as 138, *e.g.*, considerably higher than the values obtained for petroleum lubricants. Polymerization of higher olefins into lubricating oils indicates that cyclic olefins such as cyclohexene and dipentene yield polymerized oils of rather low viscosity indices. Branched-chain olefins gave polymerized oils of lower viscosity than the corresponding normal compounds.<sup>94, 95, 96</sup>

High-grade lubricating oils have been claimed by Otto<sup>72</sup> in the polymerization of ethylene at room temperature at 100–200 atmospheres' pressure and with gaseous boron trifluoride as catalyst. In general anhydrous  $\text{AlCl}_3$  is considered as an excellent catalyst in the manufacturing of lubricating oils. At low temperature the polymerization effect predominates over the splitting effect. Allenet's process claims that polymerization to lubricant hydrocarbons of high molecular weight takes place best if  $\text{AlCl}_3$ ,

is suspended in an inert solvent, for example, petroleum ether into which gaseous olefins are introduced. Introduction of olefins into middle oils containing  $\text{AlCl}_3$  showed that in addition to polymerization, condensations between the middle-oil hydrocarbon and the olefins introduced also take place. Thereby from the liquid middle oil highly viscous lubricating oils are obtained having almost the same properties as natural oil. Liquid olefins from cracked gasoline as well as light oils from coal<sup>8, 6</sup> were satisfactorily converted by  $\text{AlCl}_3$  into lubricants. The lubricating oils are claimed to be stable toward oxidation, viscous and good in color.

Polymer gasoline is the product of polymerization of gaseous to liquid hydrocarbons. This polymerization ranks among the most important catalytic processes because it utilizes cracked gases otherwise of little value by converting them with high yield into motor fuel having effective anti-knock properties. According to Egloff's statistical data, over 9 billion gallons of polymer gasoline may be produced yearly from the hydrocarbon gases of the United States, of which over 1 billion gallons may be isoöctane fuel with 95- to 100-octane rating. High-octane motor fuels are of greatest importance in high-speed aviation. Likewise the power output and load-carrying capacity of an airplane are dependent on the octane number of its fuel. It is estimated that an increase in power from 20-30 per cent results for a 100-octane fuel over one of 87-octane.<sup>23</sup> Thus polymerization of gaseous hydrocarbons occupies a significant position not only on account of economy in the use of motor fuel obtained by cracking crude oils (decreasing our reserves), but because it improves the octane rating of the refinery output, and finally provides a step in the process of making isoöctane.

The first indication of the possibility of utilizing the products of cracking as a starting material for organic synthesis such as is developed now on a commercial scale in the petroleum industry, dates back to early experiments of Ipatieff<sup>34</sup> in which ethylene was polymerized into light oils at 325° under 70 atmospheres' pressure. The oils consisted of higher olefins, paraffins and cycloparaffins. Dunstan, Hague and Wheeler<sup>22</sup> also obtained evidence that polymerization of ethylene in the presence of a catalyst leads to the formation of low-boiling hydrocarbons of high antiknock value.

Ipatieff, Corson and Egloff<sup>39</sup> developed three modifications of the process of polymerizing gaseous hydrocarbons: (1) the charging material consists of hydrocarbon gases containing propene and butene; (2) pyrolytic cracking of paraffin hydrocarbons such as butanes (and also propane) to produce olefinic hydrocarbons, which are subsequently polymerized catalytically to yield polymer gasoline; and (3) selective polymerization of normal and isobutene followed by hydrogenation of the product: octenes into isoöctanes.

Each commercial plant operated under the auspices of the Universal Oil Products Company produces about 250 bbl. of polymer gasoline by treating about 1,500,000 cu. ft. of gas per day with 38 per cent content of propene-butenes; 402 bbl. of polymer gasoline (109 bbl. pyrolytic polymer and 293 bbl. catalytic polymer) from 1090 bbl. daily charge by a combined butane cracking and catalytic polymerization process, and 347 bbl. of isoöctenes



(hydrogenated catalytically to isoöctanes) from 1300 bbl. of a butane-butene fraction by selective polymerization.

All three modifications of catalytic polymerization employ as catalyst a calcined mixture of pyrophosphoric acid on a solid absorbent-kieselguhr or a mixture of solid phosphoric acid and kieselguhr heated to 180–500° and rehydrated by heating in steam at a high temperature (Ipatieff).

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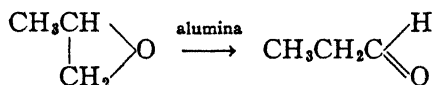
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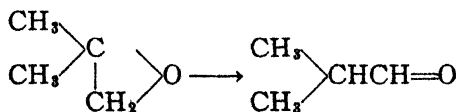
## PART IX

## Catalytic Isomerization

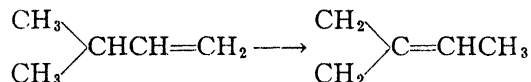
Rearrangements taking place within interacting molecules may lead to transformations resulting in the formation of isomeric compounds. As in other reactions catalysts may aid this isomerization process. Should catalytic isomerization proceed with a change in the chemical function of the reacting material, it would differ from simple isomerization in which this is not the case. Thus metameric isomerization has to be differentiated from simple isomerization.<sup>19</sup> As an example of the former is given the conversion of propylene oxide into propionaldehyde over alumina catalyst with simultaneous formation of a small amount of acetone.



Metameric transformation likewise takes place when isobutylene oxide is converted into isobutyraldehyde over alumina.

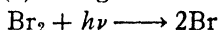


The isomerization of isopropylethylene over alumina (heated at 500–505° in a copper tube) to form trimethylethylene<sup>17</sup> is an example of simple catalytic isomerization in which a catalyst assists in the conversion of one organic compound into another isomeric with it.

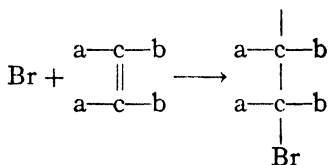


Since isomeric transformations have been experimentally ascertained for different classes of organic compounds, attempts were made to interpret them with respect to the mechanism by which they are brought about. In general, the following isomerization possibilities have been recognized: (1) direct exchange in positions of two radicals attached to one carbon atom; (2) rotation through an angle of 180° effected under the influence of certain factors, such as light, heat, catalysts, etc.; (3) formation of temporary additive compounds with chemical agents; (4) change of the covalent double linking to a semi-polar linking.<sup>39</sup> The modern explanation of inversion of geometrical isomers, developed by Berthoud<sup>3, 4, 5, 6</sup> for halogen-substituted hydrocarbons, has been expressed by an alternative non-ionic mechanism with the help of catalysts containing odd numbers of electrons, which appear to act as free radicals. Berthoud assumed the following four types of inversion:

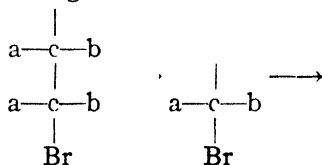
(1) halogen activation:



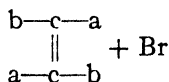
(2) atomic addition:



(3) free rotation about the single bond



(4) elimination of the Br atom and deactivation

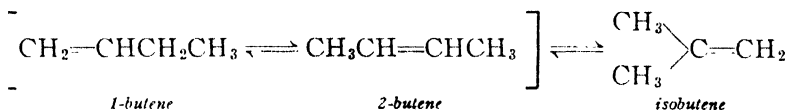


The inversion in stage (3) was supposed to occur in a molecule containing a free radical and held together exclusively by single bonds. In connection with the process of free rotation, Wolf<sup>41</sup> states that it occurs by the action of electrical forces exerted between dipolar molecules and leads to the reduction of the total potential energy. Faworsky,<sup>10</sup> discussing isomeric conversion and polymerization of unsaturated hydrocarbons, shows in a series of reactions that these conversions may be explained by intramolecular migration of the hydrogen atoms (or halogen atoms in case of halogen-substituted hydrocarbons) attaching themselves mostly in the  $\beta$ -position. Such migrations are believed to occur either in molecules which, as indicated

by their constants, are unstable and which show a high potential energy, or in molecules which are stable in themselves, but which through the presence of a catalyst make possible the migration of a hydrogen atom in one or another direction.

Sometimes there is little possibility for carbon chain isomerization without formation of highly polymerized products. Olefins undergo with great ease the following types of reaction: (1) polymerization; (2) rearrangement to isomeric hydrocarbons; (3) decomposition. Polymerization of olefins proceeding readily may suppress isomerization. With moderately high temperatures, all three reactions occur simultaneously. Under conditions of gradually increasing temperatures, the first reaction may be that of polymerization or formation of higher hydrocarbons, and with slightly more heat, isomerization and decomposition reactions may set in. Pure isomerization of olefins is thought to proceed by the shifting of hydrogen, and this results in a change in the position of the double bond or in *cis-trans* isomerization. At high temperature, and when a strong catalyst is used, there may be a rearrangement in the carbon chain as a result of depolymerization and cyclization.

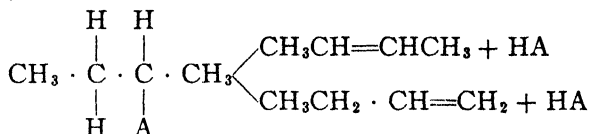
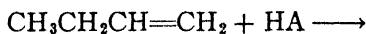
The study of isomerization of butenes has shown that 1- and 2-butenes can be interchanged and that isobutene can be isomerized to normal butenes.



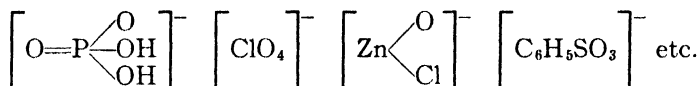
In connection with isomerization, Hurd and Goldsby<sup>16</sup> found that 1- and 2-butene rearrange with about the same ease at 600–650° and are therefore of almost the same stability. Matignon, Moureu and Dode<sup>27</sup> catalyzed isomerization of 1-butene to 2-butene by a trace of H<sub>2</sub>SO<sub>4</sub> on a pure alumina catalyst, or by a previous heating of the latter to 450°. The isomerization of isobutene to the normal isomers, as well as the reversal of this reaction, has been recorded. Frost, Rudkovsky, and Serebriakova<sup>12a</sup> obtained 28.6 per cent isobutene from pure *n*-butenes at 355°, using Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, floridin, H<sub>3</sub>PO<sub>4</sub> on charcoal and H<sub>3</sub>PO<sub>4</sub> on silicate as catalysts. N. V. de Bataafsche Petroleum Maatschappij<sup>8a</sup> used H<sub>3</sub>PO<sub>4</sub> on kieselguhr to convert *n*-butenes into isobutene. Isobutene has also been prepared from a mixture of 1-butene and 2-butene.<sup>9a</sup>

Pentene-1 and pentene-2 have been isomerized at 550–600° and therefore are equally stable. The following have been recorded also: pentene-1 converts into 2-methylbutenes at 400°; *cis*-pentene-2 into *trans*-pentene-2 in xylene at 90–100°, and *cis*-pentene-2 to *trans*-pentene-2 when exposed to ultraviolet light, the last reaction being reversible.

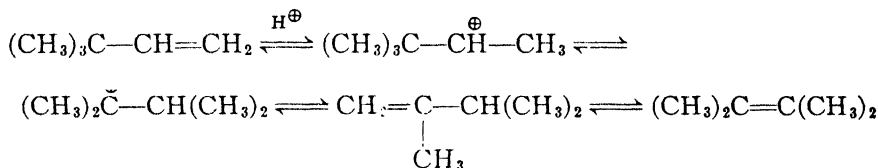
Studying isomerization of olefins, Ipatieff, Pines and Schaad<sup>21</sup> postulated the following mechanism for the isomerization of normal butenes with H<sub>3</sub>PO<sub>4</sub> catalyst: (1) formation of an addition product between the olefin and the catalyst; (2) decomposition of the addition product, whereby the same olefin or one with a different structure is split off and the catalyst regenerated:



where the A's are groups such as:

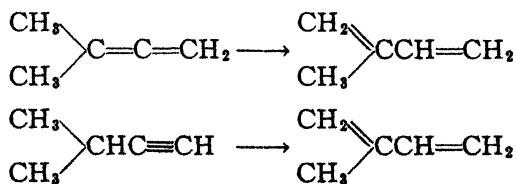


Laughlin, Nash and Whitmore<sup>25</sup> believed that isomerization of trimethylethylene may be interpreted also without the assumption of free radical formation if it is postulated that a proton is added to the double bond, leaving one carbon atom with only six electrons. The lack of two electrons in the carbon atom necessary for a stable configuration is the reason why the carbon atom induces rearrangements in other atoms, and this will result in the formation of isomeric compounds. The following scheme serves to express the above thought:

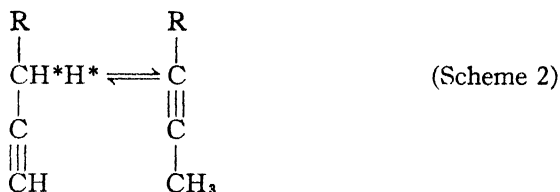


Isomerization of diolefins and an alkyl acetylene has been interpreted in the sense of shifting the position of the double or triple bond, or of converting the triple bond into two double bonds without a change in the configuration of the carbon atoms. Faworsky,<sup>11</sup> studying isomerization of acetylene hydrocarbons, found that on treatment with alcoholic potash for 24 hours at 170° propylacetylene was converted into methylethyl acetylene, which did not polymerize with sulfuric acid. This isomerization was also effected by sodium alcoholate. As a mechanism for interpreting this isomerization, Faworsky favored the one involving addition of alkali alcoholate, followed by loss of alcohol to form an allene and further reaction with the alcoholate. Such acetylenes as isopropyl acetylene would react only as far as the allene stage, and this postulate Faworsky confirmed by experiment.

It is interesting to note that the Badische Anilin und Soda Fabrik<sup>2</sup> claimed a process for preparing isoprene with a 50 per cent yield by heating isopropyl acetylene up to 400° under 50 mm. pressure in the presence of alumina catalyst. The isomeric transformation follows the scheme:







Among the other acetylene hydrocarbons, the rearrangement of 1-alkynes to 2-alkynes in the presence of alcoholic potash and the reverse action in the presence of metallic sodium have been reported by Krafft and Reuter<sup>24</sup> for 1- and 2-dodecine and 1- and 2-hexadecine.

Guest<sup>14</sup> passed a mixture containing 80 per cent of 1-heptene over soda lime in an iron tube heated to 380° and claimed that the rearrangement to 2-heptene proceeded to the extent of 70 per cent. The reverse change was brought about by heating with sodamide. The mixture obtained from the rearrangement over soda lime containing upward of 80 per cent 2-heptene was heated for 12 hours at 160° with finely divided sodamide suspended in mineral oil. After washing and distilling the final product contained 64 per cent of 1-heptene.

The findings on isomerization of paraffin hydrocarbons indicate that it usually proceeds with a rearrangement of the carbon atoms configuration:



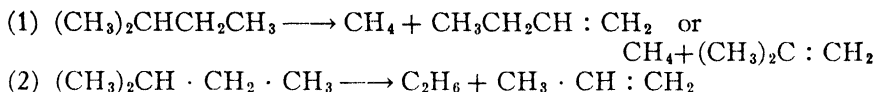
the hydrogen atom, is involved. The fact that products of paraffin isomerization contain hydrocarbons with more or less carbon atoms is considered as evidence of a complete rupture of the carbon-carbon linkage. Since both lower- and higher-boiling products are formed by isomerization of saturated hydrocarbons it is believed that in addition to the main isomerization reaction decomposition and alkylation reactions also take place. Thus the mechanism of isomerization of paraffin hydrocarbons, if it proceeds with the rupture of the C—C bond and migration of hydrogen, may be expressed as:  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2 + \text{CH}_3 \longrightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_4$ . Isomerization of paraffin hydrocarbons resulting from alkylation is expressed as:  $\text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_4 \longrightarrow \text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$ .

Finally isomerization of paraffin hydrocarbons may be brought about by free radicals, and in this case the chain is broken by alkylation:

- (1)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{—} + \text{CH}_3\text{—}$
- (2)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{—} \longrightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{H—}$
- (3)  $\text{CH}_3\text{—} + \text{H} \longrightarrow \text{CH}_4$
- (4)  $\text{CH}_4 + \text{CH}_3\text{CH}=\text{CH}_2 \longrightarrow \text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$

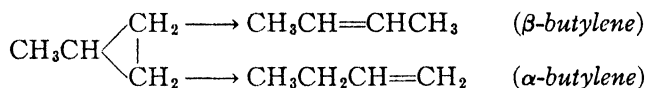
Aluminum halides appear to be the best catalyst for the isomeric transformation of paraffin hydrocarbons.

Parks, Huffman and Thomas<sup>32</sup> found a small increase in free energy with increase in the length of the carbon chain in the case of normal paraffin hydrocarbons. This increase amounts to about 600 Cal per CH<sub>2</sub> increment. These authors also found that branching of the isomeric hydrocarbons resulted in an increase of free energy. On the other hand, McKee and Ssayna<sup>28</sup> report that differences in the rate of decomposition for straight chain and branched paraffin hydrocarbons are very small, which indicates a slightly greater stability for the normal chain. Isomerization experiments with isopentane yielded products containing propane, butane and isobutylene, as well as butadiene and isoprene. The carbon-carbon bonds break during the decomposition of this hydrocarbon and the reaction proceeds in two steps as follows:<sup>7</sup>

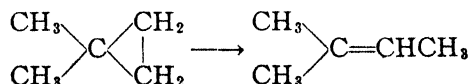


It has been stated by Frey and Hepp<sup>12</sup> that simple pyrolysis of isopentane results in the formation of *cis*- and *trans*-2-butene. In case of conversions of *n*-heptane over AlCl<sub>3</sub> catalyst at 100°, a 4 per cent yield of 2-methylhexane was obtained by Calingaert and Flood,<sup>8</sup> but no other isomeric heptanes were isolated. Petrow, Meschtscherjakow and Andrewjew<sup>33</sup> ascertained that the temperatures of isomerization and decomposition of *n*-heptane are very close to each other and that the extent of isomerization depends on the catalyst used, temperature, pressure and time of heating.

That the cyclic paraffin hydrocarbons readily undergo catalytic isomerization to form open chain olefins has been established by Ipatieff and Huhn.<sup>18</sup> The non-reactive cyclic paraffin hydrocarbon is converted into a highly reactive open-chain olefin, and this isomerization is brought about by rupture of the ring. Thus from methyl cyclopropane  $\alpha$ - and  $\beta$ -butylenes are formed:

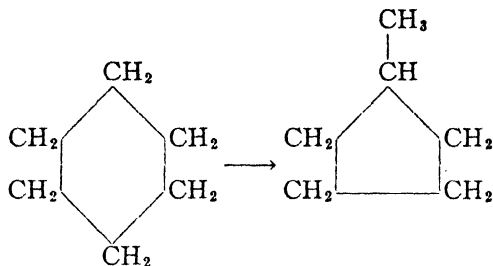


This mechanism requires a rupture of the ring and a subsequent shift of the hydrogen atom. In contrast to the carbon chain rupture, the rupture of the ring does not result in the formation of side products and this is characteristic of this type of isomerization. Isomerization of dimethylcyclopropane to trimethylethylene has been studied by Kischner<sup>23</sup> and expressed as follows:

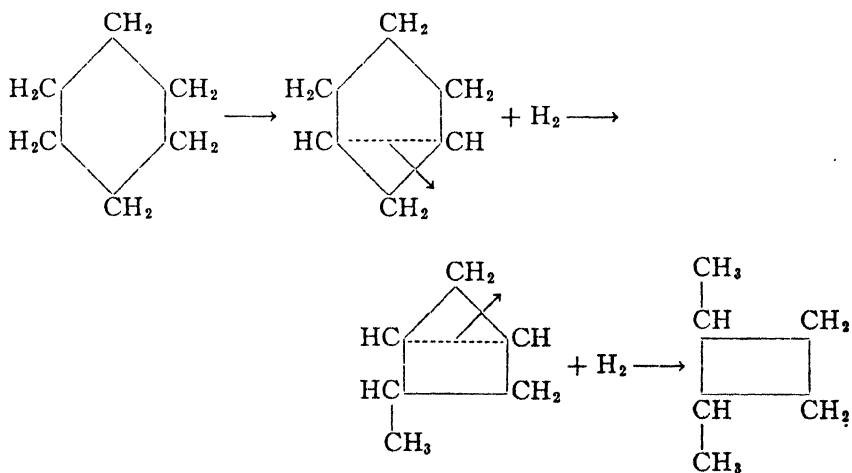


Kischner also succeeded in carrying out isomerization of cyclohexane to methylcyclopentane which is an example of isomerization by a change of the ring form.



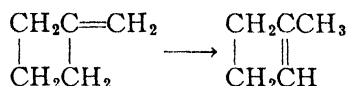


Aschan<sup>1</sup> observed the isomerization of cyclohexane to methylcyclopentane when refluxed with  $\text{AlCl}_3$ . Later Grignard and Stratford<sup>13</sup> and Stratford<sup>38</sup> studied the catalysis of cyclohexane and alkyl cyclohexanes with  $\text{AlCl}_3$  catalyst at  $120\text{--}150^\circ$  identifying the hydrocarbons of the cyclohexane series by Zelinsky's<sup>42</sup> method of catalytic dehydrogenation over Pd at  $300^\circ$ . Cyclohexane and methylcyclohexane were found unchanged, but ortho- and paradimethylcyclohexane were isomerized to the meta- compound. Paradimethylcyclohexane isomerized less readily than the ortho- compound. Nenitzescu and Cantuniari<sup>31</sup> state that isomerization of cyclohexanes in their case with  $\text{AlCl}_3$  and one per cent of water proceeded only to the formation of methylcyclopentane. Zelinsky and Turowa-Pollak<sup>43</sup> succeeded in obtaining a small amount of the isomer by heating cyclohexane with 10 per cent of anhydrous  $\text{AlCl}_3$  (or  $\text{AlBr}_3$ ) at  $120\text{--}130^\circ$  and identified the product as methylcyclopentane, together with a fraction which was believed to be another isomer, *i.e.*, dimethylcyclobutane. The formation of products was expressed by the following equation:

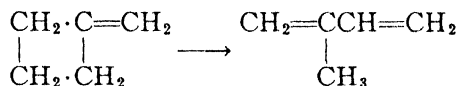


Isomerization of the simple cyclohexane derivatives (methyl, dimethyl and ethyl) to five-membered rings was obtained by Turowa-Pollak and Zelinsky.<sup>40</sup> Isomerization of a four-membered ring has been carried out in

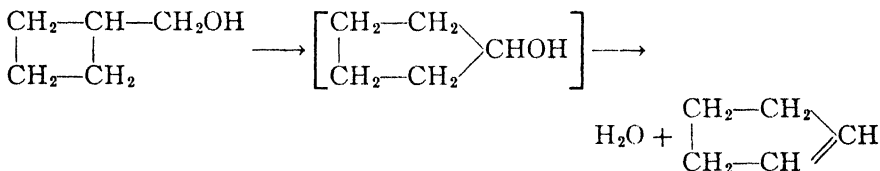
the case of methylenecyclobutane over alumina at 300°, methylenecyclobutene being formed according to the equation:



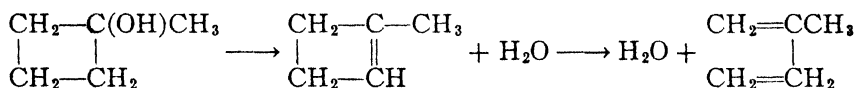
On the other hand, Dojarenko<sup>9</sup> claimed isomerization of methylenecyclobutane to isoprene over alumina at 400–430° as shown in the following scheme:



Conversion of a four-membered ring into a five-membered ring has been illustrated in the case of cyclobutylcarbinol (cyclobutanol) to cyclopentene with intermediate formation of cyclopentanol at 415–430° over alumina catalyst:

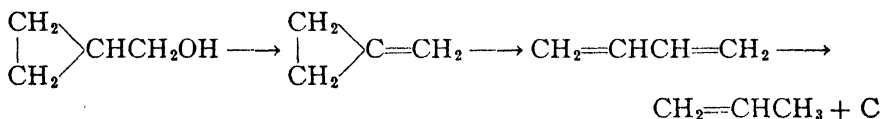


On the other hand, methylcyclobutanol with a nuclear OH group behaves differently with alumina.

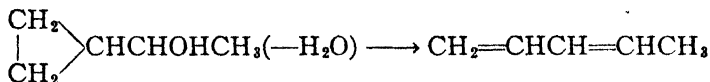


The intermediate methylcyclobutene rearranges and the chief product of the reaction is isoprene.

Cyclopropylcarbinol with a preliminary dehydration followed by a rearrangement of the resulting hydrocarbon gives propylene as the chief product, since the intermediate butadiene is not stable.



Similarly, methylcyclopropylcarbinol dehydrates first, after which the ring opens giving as the main product methylbutadiene (piperylene).

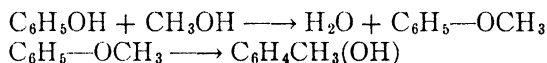


Isomerization of cycloolefins has been found to be similar in mechanism to that of cycloparaffins. However, in addition to all types of isomerization known for cycloparaffins, the mechanism characteristic of all unsaturated compounds must be added as a specific possibility of the isomeriza-

tion of cycloolefins, namely, the isomeric change introduced through the shifting of the double or triple bond.

Isomerization of aromatic hydrocarbons has been thought to be possible under the condition either that the ring is opened and a straight-chain unsaturated hydrocarbon formed, or that the double bond is shifted into the side chain, and finally through shifting of radicals along the ring when the side chain is isomerized. The first attempt to isomerize the aromatic hydrocarbons was made by Jacobsen<sup>22</sup> in the conversion of durene to trimethylbenzene and xylene with 10 per cent of  $\text{AlCl}_3$  at low temperature. This has been repeated by Smith and Cass<sup>27</sup> who discovered that treatment with sulfuric acid induced durene and isodurene to shift the methyl groups within the molecule to form 1,2,3,4-tetramethylbenzene. The saturated dimer of asymmetrical diphenylethylene was first prepared by Lebedew, Andreevski and Mantinshkina<sup>26</sup> with the aid of a catalyst such as floridin. They found that the phenylated butene dimer isomerized to the saturated cyclobutene dimer when heated at  $215^\circ$  with the same catalyst for six hours.

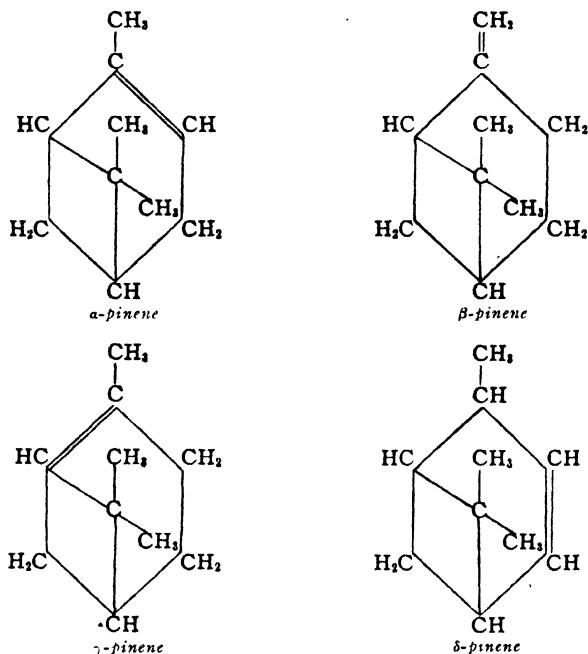
Studying the alkylation of phenols, Ipatieff, Orlow and Rasuvaew<sup>20</sup> obtained as the chief reaction product *o*-cresol and a small amount of benzene and anisol. It has been assumed that anisol is first formed and that it undergoes an isomeric transformation thus forming *o*-cresol:



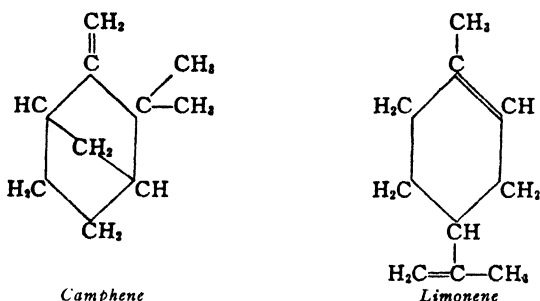
Ramart-Lucas and Amagat,<sup>34</sup> isomerizing allyl benzene to propenyl benzene over infusorial earth at  $500^\circ$ , proved the migration of the double bond in the transformation of allyl derivatives to the propenyl isomers simply by heating. Smakula<sup>36</sup> ascertained an isomerization of *trans*-stilbene ( $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_5$ ) in a hexane solution to *cis*-stilbene when subjected to the action of light. His idea was that the primary process was a loosening of the ethylene linkage by electron excitation which enabled the rotation to produce the *cis*-form. The terpenes, particularly the olefinic terpenes, such as pinene or camphene, have been studied with respect to isomerization.

The abundance of pinenes in turpentine and other inexpensive naturally occurring oils, compared to the value of isoprene obtained from pinene, account for the interest in these isomeric compounds. Harries and Gottlob<sup>16</sup> obtained a one per cent yield of isoprene from commercial *d*- and *l*-pinene by means of an isoprene lamp. However, they attributed the formation of isoprene to the limonene present as an impurity in pinene. In addition to the isoprene, gaseous compounds were separated, while heavy saturated oils of high boiling point remained in the flask. Further, it has been observed that the addition of hydrochloric acid to olefinic terpenes, *i.e.*, pinene or camphene, yields additional products which undergo isomeric changes. Meerwein,<sup>29, 30</sup> however, has established the fact that substances which undergo isomeric transformations are not the neutral molecules represented by the formula  $\text{C}_{10}\text{H}_{17}\text{Cl}$ , but rather positive ions of the type  $(\text{C}_{10}\text{H}_{16}\text{H})^+$  derived from the intermediate salt-like addition compounds of the type  $(\text{C}_{10}\text{H}_{16}\text{H})^+\text{Cl}^-$ .

Isomerization of pinenes may be expressed in the formation of the following isomers with the corresponding structure:



Since  $\gamma$ -pinene and  $\delta$ -pinene are isomerization products in theory only, the structures of camphene and limonene serve as better examples:



A few terpenes belong to the open-chain aliphatic class and others are cyclic terpenes of the cyclo-aliphatic group of hydrocarbons. Thus the type of isomerization involved in the case of terpenes depends on the class of hydrocarbons to which they belong. For instance the isomerization of monocyclic terpenes may take place by shifting of the double bond. Limonene and  $\alpha$ -phellandrene were found to isomerize to  $\alpha$ - and  $\beta$ -terpinene over  $H_3PO_4$  catalyst, while terpinolene isomerized to terpinene in the presence of halogen acid or acetic acid. In the case of bicyclic terpenes iso-

merization proceeded not only by the shift of the double bond, but also by rupture and rearrangement of the rings with the formation of monocyclic and open-chain hydrocarbons. Isomerization by double bond shift was observed over Pd black even at room temperature. In the case of polycyclic terpenes the rupture of both rings unaccompanied by any side reactions has been claimed, corresponding to a pure isomerization reaction.

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## Chapter 9

# The Role of Physical Conditions in Catalytic Reactions

### Introduction

The presence of a catalyst in a reaction mixture completely changes the conditions necessary to carry out the reaction. In addition to the type of catalyst selected, there are many other functional factors affecting the physical character of a catalytic reaction. For example, the change in the reaction velocity in catalysis is brought about not only by the function of a definite type of a catalyst, but by the initial concentration of the reactants, temperature, pressure, reaction time, space velocity of gaseous reactants, and other factors more or less specific in nature. The yield obtained in a catalytic reaction is the integral of the product of the reaction velocity by the time interval corresponding to that velocity, *i.e.*,  $\int$  velocity of the reaction  $\times dt$ .

Obviously, catalysts should possess definite characteristics with respect to the reaction in which they participate, that is, for every reacting gas or liquid of a definite composition there must be optimum space velocity, expressed in cubic meters per cubic meter catalyst per hour at definite temperature and pressure, resulting in maximum conversion. It is always desirable in itself to reduce the time of a catalytic reaction and this may be accomplished in several ways. Not all of the molecules in a system are available for chemical reaction, the total number of collisions being greater than the effective ones by a factor of  $10^{17}$ . The number of collisions initiating a reaction may be expressed by the equation:  $Z' = Ze^{-E/RT}$ , where  $Z'$  is the number of active collisions and  $Z$  the total number of collisions. The reaction velocity is related to the time necessary to complete a reaction, and increases with increase in temperature  $T$  with increase in  $Z$ , which may follow due to an increase in concentration, and a decrease in  $E$ . The activation energy factor,  $E$ , is not related to evaporation or heat of formation of the reacting molecules, but is characteristic of a definite reaction proceeding under clearly defined reaction conditions. In continuous catalytic reactions, it is possible to estimate the heats of reaction, but the heat of activation cannot be measured directly.

From the foregoing, it follows that the most influential factors with respect to the catalyst, as well as the catalytic reaction, are temperature and pressure. It should be considered further that the influence of the solvent on the state of the catalyst affects the catalytic reaction and the duration of that reaction.

### Factors Influencing Catalytic Reaction

**Temperature.**—The influence of temperature with respect to the cata-

lyst in question is discussed in the section dealing with the preparation of catalysts in Chapter 4. Concerning any catalytic reaction, it may be said that for every catalyst a definite temperature is required which produces the desired result in the highest yield. Adadurov<sup>1</sup> determined the effectiveness of a number of catalysts in the catalytic oxidation of sulfur dioxide to sulfur trioxide as shown in Table 1:

Table 1. (Adadurov).

Catalyst	Temperature	Yield (%)
Chromic oxide.	720-730 (K) (°C.)	97
Vanadium pentoxide.	670-680	98-99
Platinum.	670-870 (K) (°C.)	99
Iridium.	670-870 (K) (°C.)	26-84 (of the yield produced by Pt)
Palladium.	670-870	1-39

With respect to catalytic reactions, temperature influences are emphasized in almost every process. Increased temperature, placing increased translational kinetic energy and vibrational energy at the disposal of activation, increases the number of collisions of the molecules or atoms, enabling them to participate more frequently in chemical action. Although in some instances an increase in temperature favorably influences a catalytic reaction, in other cases the effect is the opposite. It has been stated by Milligan, Chappell and Reid<sup>36</sup> that esterification of alcohol and acetic acid over silica gel catalyst is greatly influenced by the velocity of the vapors of the reactants over the catalyst, accompanied by an increase in temperature. With increase in temperature and space velocity, esterification decreases.

Ipatieff<sup>29</sup> and Ipatieff, Jr., studying the displacement of metals from organo-metallic compounds, particularly tetramethyl lead, tetraethyl lead and tetraphenyl lead by hydrogen under high temperatures and elevated pressures, pointed out that the temperature, the initial hydrogen pressure and the duration of the experiment influenced the amount of metal precipitated:  $\text{PbR}_4 + 2\text{H}_2 \longrightarrow \text{Pb} + 4\text{RH}$ .  $\text{Pb}(\text{C}_6\text{H}_5)_4$  prepared from lead chloride and  $\text{C}_6\text{H}_5\text{MgBr}$  in an ether solution having a constant concentration of 0.001 mol per 25 cc. solvent, an initial hydrogen pressure of 60 atmospheres and a duration of 24 hours gave results as indicated in Table 2:

Table 2. Influence of Temperature on the Separation of Lead in an Ether Solution (Ipatieff and Ipatieff, Jr.).

Temperature (°C.)	Remarks	
150	Separation, begun	} from $\text{Pb}(\text{C}_6\text{H}_5)_4$
250	Separation, quantitative	
175-225	Principal reaction	
100	Separation, 15%	} from $\text{Pb}(\text{C}_2\text{H}_5)_4$
225	Separation, complete	
125	Separation, begun	} from $\text{Pb}(\text{CH}_3)_4$
250	Separation, quantitative	

When these substances were prepared in a benzene solution, the following results were obtained (Table 3):

Table 3. Influence of Temperature on the Separation of Lead in a Benzene Solution (Ipatieff and Ipatieff, Jr.).

Temp. (°C.)	--- % Lead Separated from --- Pb(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	Pb(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	Pb(CH <sub>3</sub> ) <sub>4</sub>	--- % Substance not Decomposed in --- Pb(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	Pb(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	Pb(CH <sub>3</sub> ) <sub>4</sub>
100		15.09				
125		18.10		98.0		
150	3.4	28.2	8.5			91.5
175	7.3	50.4	55.5	89.8		44.4
200	55.7	85.6	89.0	41.8	14.0	11.0
225	92.2	99.0	94.6		Trace	5.4
250	99.6		100.0	Trace		Trace

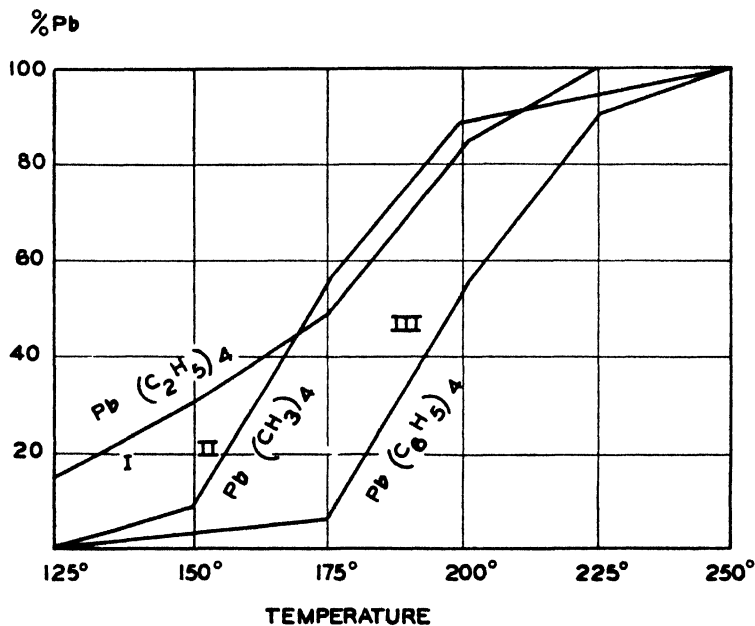


FIGURE 1.

Neumann, Kröger and Iwanowski,<sup>39</sup> studying the oxidation of carbon monoxide by oxygen ( $2\text{CO} + \text{O}_2 \longrightarrow 2\text{CO}_2$ ) over mixed catalysts ( $\text{MnO}_2 + \text{NiO}$ ;  $\text{MnO}_2 + \text{Ag}_2\text{O}$ ;  $\text{MnO}_2 + \text{Co}_3\text{O}_4$  in the ratio of 3:1, 1:1 and 1:3, respectively) at increasing temperature, other physical conditions being kept constant, found that conversions increase at first slowly and then rapidly with increasing temperature. In the system  $\text{MnO}_2 + \text{NiO}$ , the conversion curves, when a mixed catalyst is used, lie between those of the respective single components; the degree of conversion decreases with an increase in the nickel content. In the system  $\text{MnO}_2 + \text{Ag}_2\text{O}$ , the percentage yield for the 3:1 ratio lies between that of the respective single components, while the temperature-yield curves for 1:1 and 1:3 ratios lie above those for silver oxide alone. In the system  $\text{MnO}_2 + \text{Co}_3\text{O}_4$ , the degree of conversion increases with an increase in the cobalto-cobaltic oxide content. If the single oxides were arranged according to their oxygen tension at a certain temperature, then the order  $\text{Ag}_2\text{O}$ ,  $\text{MnO}_2$ ,  $\text{Co}_3\text{O}_4$ , would prevail indicating, from left to right, the decreasing catalytic activity of the oxide in question.



Hydrogenation of benzene to cyclohexane over nickel and platinum catalyst at 180–185° showed<sup>4</sup> that nickel is an active catalyst in this reaction and that the same result may be obtained with platinum, using less space velocity. An increase in temperature to about 300° decomposes cyclohexane to benzene and other hydrocarbons. In the hydrogenation of benzene over nickel at 250–300°, 75–90 per cent saturated hydrocarbons were obtained, chiefly methane at 300°, while over platinum, at the same temperature, unsaturated hydrocarbons were formed, 75 per cent at 300°; even at 450°, the amount of saturated hydrocarbons was very small.

Catalytic oxidation of ethyl benzene in a liquid phase over manganese dioxide, particularly with reference to the formation of acetophenone as a function of time and temperature, was investigated by Senseman and Strubbs.<sup>46</sup> 125 cc. of oxygen were passed over 60 g. of ethyl benzene and 0.5 g. manganese dioxide. The time of the experiment was 5.75 hours; the temperature was held at 130° for the first 45 minutes, and at 115° for the remainder of the run. The products obtained were 15.8 g. of acetophenone, 1.24 g. benzoic acid, 3.19 g. phenylmethylcarbinol, as well as water, carbon dioxide and formaldehyde. Oxidation was incomplete, as evidenced by the presence of 25 cc. ethyl benzene in the reaction products.

The role of temperature in the isomerization of butylene in the presence of alumina was studied by Matignon, Moureu and Dode.<sup>32</sup> Perret and Perrot<sup>40</sup> investigated the effect of type of catalyst and temperature on the catalytic conversion of alkaline-earth cyanides into cyanamides. At 750°, the reaction:  $\text{CaCl}_2 + 2\text{NaCN} \longrightarrow \text{CN} \cdot \text{NCA} + 2\text{NaCl} + \text{C}$  proceeds slowly.

Table 4.  
(Perret and Perrot)

Catalyst	Time (hrs.)	Yield (%)
None.	30	21
Ni, Co, or Fe, powder, 20%.	3	82
Pt, or Mn.	3	60
Ag, Ca, Li, V, Mo, W, Cr, Mg, Al, Be, C, or Si.		No action

The course of oxidation of sulfur dioxide to sulfur trioxide over vanadium catalyst is in general the same as for gases enriched with sulfur dioxide and oxygen and used in the production of sulfuric acid. The temperature interval for intensive contact catalysis was found to lie between 440 and 550°. <sup>43</sup> It was found for all sulfur dioxide concentrations that an increase in the gas velocity required a rise in the temperature to obtain optimum conversions. For equal space velocities, the increase in the sulfur dioxide and oxygen content of gases results in a small displacement of the optimum temperature conditions in the direction of higher temperatures. The use of sulfur dioxide and oxygen-rich gas in the proportion of 39 per cent of the former to 61 per cent of the latter under equal conditions per one gram of vanadium catalyst results in the oxidation of five times the amount of sulfur dioxide as compared with an ordinary gas mixture containing 7–8 per cent sulfur dioxide, 19 per cent oxygen and 73 per cent nitrogen.

Siebert,<sup>46</sup> studying the conditions in the manufacture of sulfuric acid by the contact process, using vanadium as a catalyst, found that with higher

concentrations of sulfur dioxide (up to 50 per cent) in the gaseous mixture, a space velocity of 60 volumes per minute and an increase in temperature, a decided improvement in the catalytic activity was obtained. An increase in temperature is parallel with an increase in reaction velocity and this increase in reaction velocity is accompanied, at higher temperatures, by a decrease in the poisoning effect of the catalyst.

In the condensation of propylene-benzene with sulfuric acid as a catalyst to form, for example, mono-, di-, or triisopropyl benzene, it has been ascertained<sup>51</sup> that the reaction is influenced by time, temperature and amount of the catalyst, as well as by the addition of boron trifluoride. No reaction takes place without a catalyst; at 5° temperature and under atmospheric pressure, the amount of sulfuric acid present plays a significant role. The addition of boron trifluoride, as well as an increase in the duration of the action of the reactants, increases the yield of the reaction products. A condensation of ethylene and benzene in the presence of sulfuric acid in the temperature range 10–20° does not take place; it does take place with the addition of boron trifluoride. Maximum yields of mono-, di-, or triisopropyl benzene are obtained if for every 2 mols of benzene 82 g. of sulfuric acid catalyst are used. The amount of condensation product obtained is definitely greater at higher temperatures. Further, it is stated that while diisopropyl sulfate does not act on boiling benzene, nevertheless a very rapid reaction takes place in the presence of a small amount of sulfuric acid catalyst. Isopropyl compounds, rather than *n*-propyl derivatives, are formed when the ester of sulfuric acid and *n*-propyl alcohol are treated with benzene in the presence of boron trifluoride.

It is often important that the catalyst chosen be so active that neither a higher temperature nor duration of the reaction beyond the time specified<sup>50</sup> is necessary. The catalytic activity may change during the course of the reaction as a result of the segregation of reaction products on the surface or in the pores of the catalyst, or due to accumulation of poisons. In such cases for example, in the cracking of heavy hydrocarbons, the desired degree of conversion may be obtained by increasing the temperature and pressure, or by decreasing the gas velocity. It may be that the temperature is permitted to increase gradually, the space velocity being greatly decreased, and the temperature and pressure also increased. Likewise, a pressure increase at a constant temperature and passage velocity gives the same result.<sup>25</sup> Regulation of temperature in the pressure hydrogenation of carbon-containing substances has been suggested in several patents issued to the I. G. Farbenindustrie A. G.<sup>15</sup> In the event that the desired temperature has been exceeded, the addition of ammonia is recommended, while the temperature is being lowered to the desired point. These patents specify that the amount of ammonia added should be from 5–30 per cent of the hydrogenation gas. The action of the catalyst is not influenced by the discontinuance of ammonia and the reaction proceeds normally afterwards, although it experienced a set-back in its activity during the addition of ammonia. An increase in the hydrogen content to decrease and regulate the temperature retards the activity of the catalyst.

**In any reversible chemical reaction which has reached equilibrium, an**

increase in pressure at constant temperature favors the formation of a system occupying the smaller volume and shifts the equilibrium accordingly. When the theorem of le Chatelier is applied to the equilibrium of ammonia:  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ , it is concluded<sup>41</sup> that the equilibrium mixture at any temperature will contain a greater proportion of ammonia when the pressure is high than when it is low. In the formation of ammonia by uniting hydrogen and nitrogen, the yield will be increased by working under high pressure. The pressure effect has been formulated by means of the equilibrium constant using, instead of equilibrium concentrations of nitrogen, hydrogen and ammonia, the corresponding partial equilibrium pressures:  $P_{\text{N}_2}$ ,  $P_{\text{H}_2}$  and  $P_{\text{NH}_3}$ .

$$\text{Const.} = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} \text{ or, alternatively, } K = \frac{P_{\text{NH}_3}}{P_{\text{N}_2}^{1/2} P_{\text{H}_2}^{3/2}}$$

At high temperatures,  $P_{\text{NH}_3}$  is small as compared with  $P_{\text{N}_2}$  or  $P_{\text{H}_2}$ , and if  $P$  is the total pressure of the three gases, then  $P_{\text{N}_2} + P_{\text{H}_2} = P$ . Further, when  $\text{N}_2$  and  $\text{H}_2$  are taken in the volume proportion 1 : 3, then  $P_{\text{H}_2} = 3P_{\text{N}_2}$ . Coupling this relationship with the equation for the equilibrium constant, it follows that  $P_{\text{NH}_3} = 0.325 K \times P^2$ , that is, the partial pressure of ammonia in the equilibrium mixture is, for low concentrations of ammonia, proportional to the square of the total pressure. The percentage of ammonia by volume ( $X$ ) in the equilibrium mixture is given as:  $X = \frac{P_{\text{NH}_3}}{P} \times 100 = 0.325K \times P$ ; therefore  $X$  will increase approximately in proportion to the total pressure of the reaction mixture.

Haber's experiments confirmed the foregoing, for he showed that the volume percentage of ammonia in the equilibrium mixture at 800° and a pressure of one atmosphere was about 0.012, whereas under a pressure of 30 atmospheres at the same temperature the percentage was 0.34, that is, nearly thirty times as great. However, the proportionality between the percentage of ammonia and pressure is most exact where the values of the former are low; where they become appreciable, their increase is somewhat less than proportional to the increase in pressure. That an increase in temperature is inimical to the conversion of  $\text{N}_2$  and  $\text{H}_2$  to  $\text{NH}_3$  was determined on the basis of le Chatelier's law. The combination of  $\text{N}_2$  and  $\text{H}_2$  to form ammonia is accompanied by the evolution of heat, and since an increase in temperature shifts the equilibrium in the direction involving adsorption of heat, it follows that the percentage of ammonia obtainable from the two gases decreases as the temperature increases. The influence of temperature on the equilibrium constant,  $K$ , of a reaction and its relation to the heat effect of the reaction is expressed by the thermodynamic equation:

$$\frac{d(\log_e K)}{dT} = \frac{-Q}{RT^2}$$

where  $Q$  is the quantity of heat liberated when the reaction goes to completion from left to right at the absolute temperature  $T$ , and  $R$  is the well-known gas constant.

If the relation between specific heat and temperature is known for each of the gases concerned in a gaseous reaction, then the variation of the heat effect,  $Q$ , can be formulated according to Kirchhoff's theorem:  $\frac{dQ}{dt} = C_1 - C_2$ , where  $C_1$  is the sum of the molecular specific heats of the reacting substances at constant pressure, and  $C_2$  the corresponding quantity for the resulting products. In the case of the ammonia reaction,  $C_1$  is the true specific heat at constant pressure of a mixture of  $\frac{1}{2}$  g. mol of  $N_2 + 3/2$  g. mol of hydrogen, and has been found to be  $13.47 + 0.00164t$ , where  $t$  is temperature in degrees centigrade. The quantity  $C_2$  is the true specific heat at constant pressure for one gram mol of ammonia and is given by the equation:  $C_2 = 8.62 + 0.0035t + 5.1 \times 10^{-6}t^2$ . If these expressions are inserted in the Kirchhoff formula:  $\frac{dQ}{dt} = C_1 - C_2$  and integrated, then:  $Q = Q_0 + 4.85 - 0.00093t^2 - 1.7 \times 10^{-6}t^3$  g. calories. The constant  $Q_0$  is the heat evolved in the reaction:  $\frac{1}{2}(N_2 + 3H_2) = NH_3$  at  $0^\circ$  and has been found to be 10,950 cal., so that the heat effect of the foregoing reaction at  $t^\circ$  C. is given by:  $Q = 10,950 + 4.85t - 0.00093t^2 - 1.7 \times 10^{-6}t^3$ . By inserting this expression in the equation:

$$\frac{d(\log_e K)}{dT} = \frac{-Q}{RT^2}$$

and integrating, a formula representing the equilibrium constant of the ammonia reaction as a function of temperature is obtained. Haber proposed the following formulas:

$$\log_{10} K = \frac{2098}{T} = 2.5088$$

$$\log_{10} T = 0.0001006T + 0.186 + 10^{-6}T^2 + 2.1$$

**Pressure.**—A series of established facts in catalysis indicates the great influence caused by the change from atmospheric to higher pressures. The flow through the active zone depends on the pressure drop. This suggests that whenever the flow is decreased as a result of temperature increase, the change in pressure may secure the desired reaction velocity. An increased pressure increases the time of contact with the same space velocity. For some catalytic reactions the action caused by the saturation pressure and the variance in adsorption must be taken into account.

Many reactions cannot be carried out at ordinary pressure, but high pressures make them possible. On the other hand the speed of many reactions is considerably increased when pressure is used. Many substances decompose at ordinary pressure but do not under high pressure. Introducing the high pressure factor may cause the reaction to proceed to completion. There are also cases where high pressure cannot be used. Silico-organic compounds containing phenyl radicals such as triphenyl or tetraphenyl silicons cannot be hydrogenated by heating with hydrogen under pressure at temperatures up to  $300^\circ$  with reduced nickel (these compounds are more stable than the phenyl-substituted methanes). In many

processes the alteration produced by an increase or a decrease in pressure has been a matter of special study.

Ipatieff<sup>29</sup> is the pioneer in applying increased pressures to various types of catalytic reactions and in studying the resulting effects due to the transition from atmospheric to elevated pressures. It appears that the activity of the catalyst may vary, depending on whether it is used at ordinary or increased pressure. The course of the catalytic reaction and the nature of its final product may be modified or changed in its entirety under the influence of high pressure. On the other hand, a catalytic reaction may be either accelerated or retarded. The favorable action of pressure on catalysis has been studied very frequently, particularly its increase above, rather than below, atmospheric pressure.<sup>9, 14</sup>

The course of aldehyde decomposition is greatly influenced by pressure and time of heating. Even the final products are distinctly different, depending on whether the catalysis proceeds at high or low pressures. The products of the decomposition of alcohol under pressure are paraffinic in nature, consisting principally of saturated hydrocarbons. Under ordinary pressure and at 350°, alcohol decomposes into ethylene and water, whereas under high pressure and at 400°, the only decomposition products are diethyl ether and water. The formation of ethers is characteristic of all primary and secondary alcohols when subjected to the catalytic influence of alumina, and the reaction is reversible. When dehydration of alcohol is carried out under high pressure in the presence of alumina, three products instead of two are obtained, namely, ethylene, water and ethyl ether.<sup>29</sup> In studying the decomposition of ethyl alcohol, Ipatieff concluded from his gas analysis that the higher the pressure and temperature the more completely are the reaction products reduced by hydrogen;<sup>28</sup> the course of the catalytic decomposition of alcohol does not appear to be changed by the introduction of an initial carbon dioxide pressure of 50 atmospheres.<sup>29</sup> A series of experimental observations indicates that certain liquid reactions undergo a very decided acceleration due to an increase in pressure.<sup>6, 8, 11, 16, 38</sup>

Hügel and Friess,<sup>26</sup> studying the hydrogenation of aromatic hydrocarbons under changing physical conditions, found that naphthalene does not hydrogenate over sodium hydride catalyst at 300° at ordinary pressure, but is hydrogenated at 250–350° under elevated pressure only up to tetrahydronaphthalene independently of the initial pressure. Hydrogenation takes place slowly at as low an initial pressure as 20 atmospheres. Above 350°, high-boiling yellow oils (250–350°) are obtained. Anthracene is hydrogenated very rapidly under an initial pressure of 120 atmospheres. Dibenzyl is not hydrogenated at 300° and stilbene is converted into dibenzyl above 270°.

In the catalytic reduction of tarry phenols, such as phenol, cresols, xylenols, dioxybenzenes, naphthols, as well as commercial phenol and cresols, containing oils and tar fractions, to benzene hydrocarbons, a pressure of 20 atmospheres promotes hydrogenation, the reaction going to the formation of hydroaromatic hydrocarbons.<sup>17</sup>

Laupichler,<sup>30</sup> discussing the course of the reaction in pressure hydrogenation of solid and liquid hydrocarbons and its dependence on experi-

mental conditions, emphasizes the necessity of determining the decomposition and hydrogenation velocity by its dependence on temperature and time, and the pressure dependence of hydrogen action in order to attain the optimum hydrogenation condition. Hydrogenation is believed to occur simultaneously with decomposition, and therefore the hydrogenation temperature should be that at which decomposition takes place readily. The higher the temperature, the higher the streaming velocity required.

In the hydrogenation of Ukrainian brown coal producing a benzene yield of about 20 per cent and 40–45 per cent of lubricants, the optimum conditions of hydrogenation were said to be a high initial pressure corresponding to about 130 atmospheres and temperatures up to 420°. Sometimes optimum conditions of hydrogenation coincide with a quantitative hydrogenation. Procedures and apparatus for quantitative catalytic hydrogenation under pressures of 100–300 atmospheres have been described by Adkins.<sup>2</sup>

Fischer and Küster,<sup>18</sup> investigating the influence of pressure and temperature on the synthesis of benzene and synthol over a cobalt catalyst with and without oil, found that oil assists in the uniform distribution of heat in the catalyst, but requires heating to a higher temperature. As regards pressure, it appears that with increased pressure not only synthesized hydrocarbons are formed, but alcohols as well; the latter increase in amount with increase in pressure.

Hydrogenation processes of hydrocarbons, such as benzene, hexane and cyclohexane over molybdenum catalyst at temperatures up to 450° have been studied by Griffith and Hill<sup>21</sup> with respect to the adsorption of hydrogen, as well as of hydrocarbons on the catalyst. These investigators state that the adsorption of hydrocarbons at ordinary pressure has a maximum at the same temperature at which a maximum occurs for the activity of the catalyst; the minimum adsorption of hydrocarbons for high pressure is related to the structure of the catalyst. A special treatment has been suggested<sup>27</sup> for catalysts intended for use in pressure hydrogenation. For example, various metal sulfides are heated with sulfur-containing volatile hydrocarbons at atmospheric pressure in the presence of a large amount of hydrogen; at higher pressures, they may be subjected to a still greater amount of hydrogen.

Ipatieff found that a higher temperature is required to cause the aldehyde decomposition under high pressure than is necessary at ordinary pressure:  $\text{RCH}_2\text{OH} \longrightarrow \text{H}_2 + \text{RCHO}$ ;  $\text{RCHO} \longrightarrow \text{RH} + \text{CO}$ . In this case pressure decreases the catalytic action of the iron used as a catalyst. In some cases catalytic decompositions under applied pressure in the presence of a catalyst may differ from those taking place under normal pressure. Ipatieff has shown that in some cases products are formed at higher pressures that are not liberated otherwise. In the decomposition of alcohol under pressure, the main influence appears to be the absence of the formation of carbon which may separate in this reaction and combine with hydrogen to form methane. At ordinary pressure, ethanol decomposes in an iron tube at a temperature above 520°, but with carbon deposition.

Likewise Ipatieff's researches prove that the gaseous products obtained are predominantly saturated hydrocarbons (from  $\frac{2}{3}$  to  $\frac{3}{4}$ ), sometimes mixed with a considerable amount of carbon dioxide. In studying the course of the decomposition of organic compounds Ipatieff constructed curves expressing the relationship between pressures developed by heating and the time of heating, pressures being plotted as the ordinate and time as the abscissa. The most characteristic value of the course of decomposition of a given compound was found to be not the average pressure increase during the reaction, but the maximum velocity of pressure increase denoted by  $(dp/dt)_{\max}$ . Ipatieff considered this value geometrically as the tangent of the largest angle formed by the tangent to the curve and the abscissa axis;  $(dp/dt)_{\max}$  multiplied by the time necessary to bring about the maximum pressure ( $p_{\max}$ ) is found to be constant for a whole series of temperatures in the case of alcohols:  $(dp/dt)_{\max} \times t = K$ . The constant  $K$  changes, however, for different catalysts.

Tammann and Pape<sup>48a</sup> studied the influence of pressure upon the velocity of polymerization. It is emphasized that the influence of pressure upon the polymerization of systems such as isoprene, vinyl acetate, dimethylbutylene and indene is much greater than for most reactions. These polymerizations have been shown to be monomolecular reactions, and this might be explained if one assumes that the preliminary changes take place in individual molecules before they combine. In each case studied it has been established that a decrease in volume occurs under the influence of polymerization; therefore it follows that the decrease in pressure at a constant volume might be taken as a measure of the reaction velocity. If the pressure increases, the temperature at which the polymerization starts decreases.

**Solvents.**—The nature of the solvent used for the catalyzed substance has been found to affect materially the reaction velocity of the catalytic process. Halban and Hecht<sup>22</sup> and Halban and Kirsch<sup>23</sup> observed in the catalytic decomposition of benzyl xanthogenic acid that the substitution of carbon bisulfide for methyl alcohol as solvent increases the velocity  $1\frac{1}{2}$  million times.

Taipale<sup>48</sup> definitely established the fact that the structure of the molecule and the solvent among other conditions affect the velocity and the direction of the catalytic addition of hydrogen. Moelwyn-Hughes and Hinshelwood<sup>37</sup> reported that trinitrobenzoic acid decomposes in water 2000 times faster than in toluene. The velocity in establishing equilibrium between keto-enol tautomers have different values for different solvents.<sup>34</sup> The catalytic effect of solvents has been ascertained in the conversion velocity of camphenecchlorhydrate into isobornylchloride and bornyl chloride in the racemization of optically-active isobornyl chloride or other halogen alkyls<sup>5</sup> in the alcoholysis of camphenecchlorhydrate and triphenyl-chlormethane,<sup>33</sup> as well as in the decomposition of malonic acid.<sup>7</sup> In the first case Meerwein and van Emster interpreted the observed acceleration by the solvent in the conversion of bornyl chloride into camphenecchlorhydrate by recognizing the dielectric properties of the solvent and with them the

increasing ability for ionization of the dissolved substances as an essential factor in bringing about the phenomenon.

The reaction accelerating influence of solvents has been thought of in the light that the velocity of transition of the reacting molecules from a homopolar into a heteropolar or into an ionized form is extraordinarily increased in a medium inclined to polarization; the velocity of conversion is likewise increased. Furthermore, the intermolecular rearrangement, namely, the electronic displacement with simultaneous bond migration, proceeds considerably more easily for the ions originating on dissociation than for the normal molecules of the initial reaction. The role of the solvent is to convert the reacting molecules into a reactive state, and this should occur more readily the higher the dielectric constant of the solvent, whereby the rearrangement takes place as spontaneous stabilization of the complex molecule set free and appearing as a cation. But cases are encountered in which the specific velocity increase due to the solvent does not parallel the dielectric constant of the solvent. In this event the effect of the solvent has been linked with the solvation of the dissolved reacting molecules and connected in itself with a change in chemical behavior reflected in a displacement of equilibria and reaction velocities. A solvent may exert also a retarding action on the catalytic process and this has been connected by different investigators with different properties of the solvent such as solubility,<sup>13</sup> refractive index,<sup>12</sup> viscosity,<sup>24</sup> cohesion,<sup>47</sup> and dielectric constants.<sup>36</sup> No general interpretation exists for the accelerating or retarding action of solvents. A catalytic impulse may be a function of less general factors in the experimental conditions of a catalytic process than temperature, pressure, time and solvent factors.

Manchot<sup>31</sup> referred to the addition of alcohol within definite concentration showing an increase in the catalytic oxidation of alcohols. Goldschmidt and Pauncz<sup>20</sup> emphasized in their study of peroxidation and catalytic action of ferro-salts that, in addition to the impulse produced by the peroxidate, a catalytic impulse always takes place, this being measured by the oxygen development. The catalytic action was found to decrease with increasing pH. The oxidation maximum for alcohol lies at pH = 0.7 and has the highest peak for Cl' and the lowest for SO<sub>4</sub>". The peroxidation action of hydrogen peroxide in the presence of Fe" salts in the case of alcohol is explained by the assumption of a chain reaction formed by a reaction able to peroxidate intermediate compounds of the Fe" salt, which in its turn oxidizes the reacting substance (alcohol) and gives back the Fe" salt; when the transition to Fe''' takes place, the chain tears off.

Pissarjewsky and Gluckmann<sup>42</sup> studied the influence of the solvent on the catalytic decomposition of hydrogen peroxide solution over platinum, and also over manganese dioxide on charcoal, as catalyst. The solvents used were water, ether, ether-water and acetone. Catalytic decomposition in aqueous solutions proceeds monomolecularly. The kinetics change greatly in ether-water solutions and the reaction velocity is always greater than in pure water or pure ether. The most important factor in the influence of the solvent on hydrogen peroxide decomposition is postulated to be the action in space effected by the solvent. This action superimposes on



the influence of the mutual action of molecules of the solvent with ions of the metal acting as a catalyst, which leads to the formation of solvates of ions participating in this or that manner in catalysis. The solvation of molecules of hydrogen peroxide by its adsorption through the catalyst apparently plays no special part. By using acetone as a solvent which, unlike ether, is miscible in all proportions with water, Gluckmann<sup>19</sup> ascertained that water accelerates the reaction but that the presence of 10–15 per cent of water is necessary to produce the same effect in this case as 0.7 per cent in ether.

A small change in the concentration of water dissolved in ether (0.7–1.2 per cent) has a very great effect on the reaction velocity (20–30 fold). The attainment of an equal change in the acetone solution requires a much greater addition of water, namely, up to 80 per cent. The curves illustrating the dependence of the reaction velocity on the water content have a maximum in the case of ether, but this is not observed in the case of acetone.

An increase in the hydrogenation velocity has been effected in a process of solidifying crude oil over a suspended powdered nickel catalyst (0.024 per cent) by applying a high voltage alternating current and producing thereby an electric stirring. To retain the catalyst in the reaction chamber for use in the hydrogenation of another charge of oil after the end of the reaction, alternating current is replaced by direct current.<sup>44</sup> A similar result was obtained in the conversion of nitrobenzene into aniline over one per cent metallic nickel in 5 hours when subjected to an 18,000-volt alternating current.

Cococinskii<sup>10</sup> observed an electrostatic charge on the platinum catalyst placed in an electrically heated copper tube in the catalytic oxidation of ethyl alcohol. He assumed that, through the greater mobility of positive ions, an agglomeration of negative ions on the catalyst surface takes place and during the reaction an adsorption compound originates, which influences the electrostatic equilibrium in the sense of favoring the ionization. It was Brewer's observation that ions are formed in the oxidation of alcohol by air. Cococinskii's experiment showed that actually, as a result of the reaction, the catalyst accumulated a charge equivalent to 1.3 to 13.0 volts. He pictures the course of the reaction as follows: on the contact surface are present activated oxygen atoms which react in pairs with one alcohol molecule to form a complex having on the surface two hydroxyl groups; as a result of their decomposition a negative water ion is formed. Whether other ions are parts of the alcohol molecule is not certain.

Bailey and Taylor<sup>3</sup> found, in an investigation of the reaction between potassium permanganate and hydrogen peroxide in an acid solution, that stirring has an important influence in the regions of high concentrations of the peroxide. Assuming a catalytic action of the manganese ions, it is obvious that for high concentrations of hydrogen peroxide these ions are very active catalysts, while for small concentrations they have relatively little influence. By stirring, the local agglomeration of manganese ions is hindered and likewise an increase in their action is made impossible; thus a slowing down of the chemical reaction follows.

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## Chapter 10

# Classification of Catalysts with Respect to Type of Reaction

For the purpose of a clearer presentation of experimental evidence of various catalytic reactions in organic and inorganic chemistry, the material has been presented in the form of tables. From these tables the reader will become acquainted with all the specific types of reactions which have been extensively studied. One will learn also about the physical conditions and the type of catalysts which have been used to effect chemical changes in definite types of reactions and in compounds of definite molecular and atomic structure. In this manner a cross-section of the accumulated knowledge of catalytic reactions may be obtained, analyzed, and possible generalizations drawn.

The types of catalytic reactions recorded in the tables are: (1) Synthesis; (2) Decomposition; (3) Hydration; (4) Dehydration; (5) Reduction; (6) Oxidation; (7) Hydrogenation; (8) Dehydrogenation; (9) Halogenation; Chlorination, Bromination, Fluorination, Iodination; (10) Sulfurization; (11) Desulfurization; (12) Alkylation; (13) Condensation; (14) Polymerization, and (15) Isomerization.

### Selective Action of Catalysts

A major problem in catalytic chemistry is to establish a method for the choice of catalysts for a particular type of reactant, as well as a particular type of reaction instead of the empirical method used at present. A careful analysis of the tables should indicate whether or not definite catalysts or groups of catalysts can be specified for definite types of reactions. The question may be asked, Is the type of the reaction, the nature and structure of the reactants participating in it, or the individual characteristics of the catalysts and their specific functions the dominating factor in the choice of catalysts?

An attempt has been made to approach the solution of this problem by comparing groups of catalysts specific for various catalytic reactions in general (Table 1). From this table the groups of elements of the Periodic System active as catalysts in a particular type of reaction have been deduced (Table 1a). Groups of catalysts specific for various reactions of single compounds are presented in Tables 2, 2a, 2b, 2c, 2d and 2e. Tables 3, 3a, 3b, 3c and 3d permit comparison of groups of catalysts typical of reactions of saturated hydrocarbons (paraffins), unsaturated hydrocarbons (olefins, acetylene), aromatics and terpenes. Groups of catalysts characteristic for reactions of aldehydes, ketones, acids, alcohols, nitro-compounds ethers and esters are given in Tables 4, 4a, 4b, 4c, 4d, 4e and 4f. Finally,

groups of catalysts suitable in reactions of various oils, coal, tar and wood may be found in Tables 5, 5a and 5b.

These are a few examples in which the knowledge presented in the tables of various reactions in catalytic chemistry of organic and inorganic compounds may be used and various comparisons drawn. Catalysts may be classified also according to their inherent functions as carriers, as agents assisting in loosening bonds and as instrumental in forming intermediate addition compounds. The primary changes with aluminum chloride, for example, in hydrocarbons, may consist in an activation of the hydrogen atoms leading, in some cases, to a loosening of certain bonds. The activation of hydrogen atoms is expressed in hydrogenation and dehydrogenation, and also in condensations in the aromatic series, in cracking and exchange reactions. The migration of halogen atoms in carbon chains and rings under the influence of aluminum chloride is expressed in isomerization reactions. Magnesium and titanium oxides, clays and naturally occurring earths favor scission of the C—C bond. Catalysts acting as carriers in the gaseous phase and used in the reaction are most typical for halogenation reactions. Certain catalysts are able to form double salts with the reactants, and, in this case, the stability of the intermediate addition compounds determines their catalytic action.

It appears likely that the function of certain types of compounds as catalysts may be traced back to their chemical and physical properties. For instance, the relationship between chemical and physical properties of oxides and their catalytic effect may be viewed in the sense (1) of varying degrees to which they are reduced during the catalytic reaction (lower oxides, metallic state, carbides, or hydrides); (2) of varying surface changes due either to thermal effect or chemical reaction, and (3) of varying extent of dehydration, etc. In some catalytic reactions, the use of oxides having many oxidation steps are most appropriate. Elements of the even series (4th and 6th groups of the Periodic System) resemble one another more than successive members of the odd series (5th and 7th groups). The lower oxides of the last members of the even series resemble in many ways the first members of the odd series. Thus basic oxides of chromium and manganese are in many ways similar to the oxides of copper and zinc, and this may prove significant in the similarity of their action as catalysts. In some catalytic reactions difficultly reducible oxides are more suitable than the readily reducible oxides; in others, on the contrary, the latter are favored. In still other reactions a mixture of both can be used to the best advantage.

Cupric oxide, nickel monoxide and ferric oxide have strong catalytic action, effective at low temperatures, are less stable thermally and more easily reduced, so that more of their catalytic action may be due to the presence of metal (*in statu nascendi*) than to the oxide. Alkalies and lighter alkaline earth oxides are stable at high temperature, do not exert a powerful catalytic effect, and effectively catalyze surface reactions. To this group of oxides also belong naturally occurring clays and mixed oxides. In the choice of a catalyst, it is important sometimes to differentiate between

basic oxides and those exhibiting acidic properties. The oxides and hydroxides of copper and gold, for example, are feebly basic.

The isomorphism of silver and sodium sulfates, cupric salts with iron cobalt and nickel may explain their equal catalytic properties in certain reactions. Also to be considered is the fact that the properties of gold are similar to those of the platinum group, and silver to the mercury group.

The chemical activity of and affinity for oxygen is to be taken into consideration in the case of certain catalytic reactions. From this point of view, elements with large atomic volumes are usually associated with great chemical activity and affinity for oxygen, while elements of small atomic volumes have a weak affinity for oxygen. Alkali metals have the largest atomic volumes or the largest spaces between the atoms (lithium < sodium < potassium < rubidium < caesium); and boron (carbon), aluminum (magnesium, silicon), cadmium (copper, iron), nickel, ruthenium (molybdenum, palladium), cerium have the smallest atomic volume. The electro-affinity, whether weak or strong ions are involved, plays a part in the choice of catalysts. Strong ions such as  $K'$ ,  $Na'$ ,  $NO_3'$  and  $Cl'$  hold their charges tenaciously, while weak ions such as  $Hg''$ ,  $Ag'$ ,  $OH'$  and  $Cu'$  lose their charge readily.

Differentiation of groups of catalysts capable of performing definite functions would undoubtedly be of great assistance in effecting joint action of catalysts on one side and continuity of two or three different catalytic processes on the other. Combining two or three processes in sequence through successive application of catalysts specific for the single process is of great significance, since chemical reactions between products obtained *in statu nascendi* would be more efficient. Likewise, the adjustment of physical conditions, such as temperature and pressure, would be easier and effect greater economy in certain cases of continuous and joint processes (hydropolymerization, polymerization-isomerization. etc.).

## PART I

### Catalysts for Various Types of Reactions

Table 1. Groups of Catalysts for Catalytic Reactions in General.

Synthesis	Hydration	Dehydration (Continued)
Fe (Ni, Co). Cu (Ag). Zn, Cr (Mn). Chiefly oxides. Double salts. Alloys. Hydroxides, carbonates. Chromyls, carbonyls. Perchromates, perborates.	Oxides (Al, Th, W, Mo, Ti, Cr, Zn, Cd, Hg, Fe). Double salts of Th and alkali (alkaline earths). Complex salts (Fe, Co, Ce). Acids ( $H_2SO_4$ , $H_3PO_4$ ). Halides (Al, Cd, Zn). Oxalates (Au, Ag, Cu, Fe, Ni, Co, Cr). Acetates (Zn). Carbonyls (V, W, Mo). Metaphosphates (alkalies, alkaline earths) on kieselguhr. Hydrates (Fe, Al, Hg, or Si). Melts of chlorides (Ca, Zn, Mg). $Ag_2SO_4$ , $Ag_2S$ . Dehydrated japanes acid ton.	$H_3PO_4$ . Silicates and hydrosilicates (Al). Aluminates (Na). Alone, or as carriers, are used: kaolin, bleaching earth, japanes acid earth, infusorial earth, florida earth, birch wood, alundum, graphite, coke.
Decomposition	Dehydration	Reduction
Metals of the Fe group (Fe, Ni). Oxides (Fe, Ni, Cu, W, U, Ti, Zn, Al, Mo, Cr, Th, U, alkaline earths). Metals of the Pt group: Pt, Pd, Os, Rh, Ir, Ag. Chlorides (Zn, Sn). Carbides (Fe, Ni, Mo). Carbonates (Na, Ca). Hydroxides (La, Ce, Pr, Nd, Y, Zr, and Th). Melts (Mg, Ni, Ag, Cu). Alloys Cu (Pd, Au).	$Al_2O_3$ and oxides (W, Si, Th, Mn, Zn, Ti, Zr, U, Pb, Fe, Ni, P, Ce). Phosphates and metaphosphates (Mg, Ca, Na).	Metals (Ni, Cu, Fe, Co, Pd, Pt, Mg, Zn, Ag, Au, Pb, Sn, Hg). Oxides (Al, Ni, Mn, Mg, Mo, Cr, Th, Ba, W, V, Cu, Zn, Si, Ti, Se, Pt). Alloys: Cu-Cr, Zn-Cr, Ni-Mg, Fe-Cu, Co-Mn. Mixtures of metals (Ni) with oxides (V, Mo, Zr, Si, Al, Cr) or (Cu) with oxides (Cd, Co, Zn, Sn, Mg, Mn). Ni (formate, carbonate, nitrate). Cu (acetate, chromite, chromate). Cu-Ba (chromate).

Table 1 (Continued).

Reduction (Continued)	Hydrogenation (Continued)	Fluorination
Hydroxides (Cu, Co, Fe). Chlorides (Sn, Zn). Cd (chromite). Pd (sol). Bone charcoal, active charcoal, graphite, pumice, kieselguhr, silica gel, Al or double silicates, active alumina, infusorial earth, fuller's earth.	MoO <sub>3</sub> +CuO. MoO <sub>3</sub> +S. MoO <sub>3</sub> on brown coal. MoO <sub>3</sub> (MoS <sub>3</sub> ) mixed with oxides (Zn, Mg). MoS <sub>3</sub> , MoS <sub>2</sub> (on charcoal). Mo polysulfide on charcoal. WO <sub>3</sub> tungstic acid. W with Cr <sub>2</sub> O <sub>3</sub> or ZnO. WS <sub>3</sub> (on charcoal, ceramic mass). NH <sub>4</sub> sulfo tungstate. Heteropolymer acids containing Mo, W. Sn (melted). Sn (chloride, oxalate, oxyhydrate, acetate, formate, tetraphenyl). Zn dust. Zn (oxide, propionate, butyrate).	Metal halides on active charcoal. SbCl <sub>3</sub> , Sb in a liquid state. Hg (oxide, chloride, fluoride).
Oxidation	Dehydrogenation	Iodination
Pt, Pt alloys (Pt-Ag, Co, W, Rh, Ir, Ru). Fe, Cu, Ag, Ni, Co, Mn, Hg, C. Metals on carriers: ton, Mg quartz, asbestos (Pt), puzzulolana earth, zeolites, pumice. Oxides (Fe, Co, Mn, Cr, Cu, V, Si, Ti, Th, Al, Mo, Nb, Ta, Ni, Mn, Hg, Ag). Mixtures: metals+oxides, or oxides+oxides, also on asbestos, pumice, carbides. Vanadates (Sn, Bi, Ag, Ca, Mo, Cr, Cd, NH <sub>4</sub> , Co, Pb, W, Fe). Carbonyls (Fe, Na, K). Carbonates (Li, K, Ni, Co). Chromites (Cu, Zn, Fe). Volatile halides (HCl, HI, HBr, CH <sub>3</sub> Cl, CCl <sub>4</sub> , NH <sub>4</sub> Cl). Mn, Fe, Cu, Ni, Zn. Hydroxides (Fe, NH <sub>4</sub> ). Borates (Co, Mn). Molybdates (Cu, U). Acetates (Ag, Mn, Co, Cr, Na, Ni). Stearates (Mn, Zn). Butyrate (Mn).	Pt, Pd (black, on asbestos, active charcoal) (Al <sub>2</sub> O <sub>3</sub> best carrier). Os, Re, Ru. Cr (oxide+difficultly reducible oxides Al, Zr, Ti, Si, Th, Mg and readily reducible oxides Be, Pb, or Hg). Cr oxide gel. Mo (MoO <sub>3</sub> ). Molybdates of heavy metals (Cu, Ag, Fe, Ni). Cu, Cu (oxide, hydroxide). Cu+(Ce, Zr, Zn, U, Ca, Ba, Sr). Mixtures: Cu+Cr+Mg. Cu+H <sub>2</sub> PO <sub>4</sub> . NaHPO <sub>4</sub> or Ba <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> . Cu+(Cr, Mn, Mg oxides). Cu-Mg alloy. CuO on pumice, charcoal. Zn (oxide, hydroxide, chloride, sulfide, molybdate, nitrate, arsenate, telluride, selenide, phosphide). Zn (on Al <sub>2</sub> O <sub>3</sub> , pumice). Ni (on Al <sub>2</sub> O <sub>3</sub> ). Ni sulfide. Ni+(Na <sub>2</sub> O, NaNO <sub>3</sub> ). Ni-Mg, Ni-Cu alloys. Ti (Zr, Ce, Th) nitrates on Al <sub>2</sub> O <sub>3</sub> . NH <sub>4</sub> (tungstate, vanadate) on charcoal.	I, BF <sub>3</sub> , HCl, Al <sub>2</sub> O <sub>3</sub> . CH <sub>3</sub> COOH and buffer acetate solution. KHC <sub>2</sub> O <sub>4</sub> .
Hydrogenation	Chlorination	Sulfurization
Ni, Pd, Pt. Fe, Co, Cu. Mo, W, Sn. Ni, Ni-Co, Ni-Cu (alloy). Al <sub>2</sub> Ni alloy. Ni-Mo, Ni-Al <sub>2</sub> O <sub>3</sub> -ThO <sub>2</sub> , Ni-Pd. Ni-Zn, Ni-CeO <sub>2</sub> . Ni-Al, Ni-Cr, Ni-Mg. Ni-Pt. Ni (carbonate, oxide, hydroxide, chloride, sulfate, formate, borate, chromite, sulfide, carbonyl, nitrate, acetate, silicate, tungstate, oxalate, butyrate, oleate, benzoate). Ni or NiO on kieselguhr, bone charcoal, ton, wood charcoal, alumina, chamotte, asbestos, silica gel, pumice, fuller's earth and Japanese acid earth. Pt (Pd) colloidal, black, oxide, sulfides, chlorides, chromates, also on carriers (charcoal, silicic acid gel, ton, pumice, Ni, Pt, asbestos, bone and blood charcoal, kieselguhr). Fe (Co) (powder, filings). Fe-Cu, Fe-Al. Fe-Sn, Fe-Mo. Fe+chlorides (Mg, Cr, NH <sub>4</sub> , Ni). Fe (oxide, hydroxide, sulfide, sulfate, acetate, lactate, formate). Mixtures Fe (oxide, hydroxide)+metal oxides. Cu, Cu-(Ag, Al, Zn, Ni) alloys. Cu-Zn chromate, Cu-Zn-Cr.	Adsorbents (active charcoal, silica gel, Al gel, bleaching and Florida earths, diatomite, asbestos, kieselguhr, bauxite, coke, etc.) impregnated with halides of heavy metals: ZnCl <sub>2</sub> , FeCl <sub>3</sub> , FeBr <sub>3</sub> , FeI <sub>3</sub> , SbCl <sub>3</sub> , SnCl <sub>2</sub> , HgCl <sub>2</sub> , BiCl <sub>3</sub> , CuCl <sub>2</sub> , AlCl <sub>3</sub> , MgCl <sub>2</sub> . Melts of metal chlorides (eutectic mixtures of AlCl <sub>3</sub> , NaCl, FeCl <sub>3</sub> , CuCl <sub>2</sub> ). Double salts: AlCl <sub>3</sub> ·FeCl <sub>3</sub> , I-Fe (very active). Oxides: Ti, Si, Si-Fe, Al (gel grains).	Hg (HgSO <sub>4</sub> ). V (V <sub>2</sub> O <sub>5</sub> ). Sulfates (Ca, Fe, Cu, Al, Na, Ni, Ag). Dimethyl sulfate. Sulfides (Ca, Ba, Mg, Mn).
Hydrogenation	Dechlorination	Desulfurization
Cu (oxide, hydroxide, carbonate, chromate, acetate, lactate). CuO+MoO <sub>3</sub> . Cu+ZnO+Cr <sub>2</sub> O <sub>3</sub> . Cu on silica gel, kieselguhr, pumice, charcoal, Al <sub>2</sub> O <sub>3</sub> , chamotte. MoO <sub>3</sub> , MoO <sub>3</sub> . (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> on active charcoal, SiO <sub>2</sub> , molybdic acid.	Chlorides (Ba, Ca, Zn). Oxides (Ti, Cu). Fe powder. Na, Mg, Zn.	Highly porous active substances: silica gel, bauxite, charcoal, kieselguhr, asbestos, porous lime, Florida and fuller's earth. Metal sulfides and oxides. Mo (oxide, sulfide) on alumina gel. Na, Pb, Co, W, Ni, Cr (sulfides, oxides). Oxidizing substances. Mixtures: NiO+(CoO, Cr <sub>2</sub> O <sub>3</sub> , ThO <sub>2</sub> , WS <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> ). Ni thiomolybdate sponge + Na <sub>2</sub> Al <sub>2</sub> O <sub>4</sub> . Ni+Bi on silica gel. Cr <sub>2</sub> O <sub>3</sub> +(Fe, MnCl <sub>2</sub> ) on active charcoal. Fe, Fe ore. Fe (chloride, sulfate, hydroxide) on active charcoal. Cu (oxide, chloride, carbonate, chromite, hydroxide, acetate). MgO+ZnO+MoO <sub>3</sub> +MoS <sub>2</sub> ( <i>in statu nascendi</i> ).
Hydrogenation	Bromination	Nitrogenation
	Metal bromides mixed with active charcoal, silica gel, Al gel). HBr, IBr, MgBr <sub>2</sub> , BeBr <sub>2</sub> , ZnBr <sub>2</sub> , CdBr <sub>2</sub> , SbBr <sub>3</sub> , AlBr <sub>3</sub> . Organic bromides: acetyl bromide, C <sub>2</sub> H <sub>5</sub> Br, C <sub>4</sub> H <sub>9</sub> Br, C <sub>6</sub> H <sub>5</sub> Br.	Charcoal, silica gel. H <sub>2</sub> SO <sub>4</sub> (75 g.)+HNO <sub>3</sub> (50 g.). CaCN <sub>2</sub> , CaCl <sub>2</sub> . KOH·K <sub>2</sub> CO <sub>3</sub> .
Hydrogenation	Denitrogenation	Alkylation
	Cu powder. Cu suboxide.	AlCl <sub>3</sub> , BF <sub>3</sub> . ZrCl <sub>4</sub> , ZnCl <sub>2</sub> . H <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> PO <sub>4</sub> . P <sub>2</sub> O <sub>5</sub> (anhydrous) with activators: HS, HCl, HBr, HF, HCN, H <sub>2</sub> O. Activated silicates, bleached earth, clay, kaolin. FeCl <sub>3</sub> (anhydrous). Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub> . AlBr <sub>3</sub> , ClO <sub>4</sub> . Destructive alkylation. AlCl <sub>3</sub> , H <sub>2</sub> PO <sub>4</sub> .
Hydrogenation	Condensation	
	Basic oxides: Al <sub>2</sub> O <sub>3</sub> , UO <sub>2</sub> , ThO <sub>2</sub> , CaO, BaO, MgO, SrO, or Li <sub>2</sub> O, V <sub>2</sub> O <sub>5</sub> , ZrO <sub>2</sub> , SiO <sub>2</sub> . Chlorides. AlCl <sub>3</sub> , ZnCl <sub>2</sub> , FeCl <sub>3</sub> , SnCl <sub>2</sub> , MgCl <sub>2</sub> , ZrCl <sub>4</sub> , CuCl <sub>2</sub> +C <sub>2</sub> Cl <sub>2</sub> . BF <sub>3</sub> (other Friedel-Crafts agents). AlCl <sub>3</sub> , ZnCl <sub>2</sub> on (bentonite, fuller's earth). Surface active substances: silicates, silica gel, alumina, kaolin, kieselguhr, hydrosilicates (bleaching earth), bauxite, permutite.	

Table 1 (Continued).

<i>Condensation (Continued)</i>	<i>Polymerization (Continued)</i>	<i>Isomerization (Continued)</i>
H <sub>2</sub> PO <sub>4</sub> , P <sub>2</sub> O <sub>5</sub> (on fuller's earth, silica); P <sub>2</sub> O <sub>5</sub> on kieselguhr.	HClO <sub>4</sub> , molybdic acid.	ZrCl <sub>4</sub> .
Ag phosphate dissolved in H <sub>2</sub> PO <sub>4</sub> .	Double salts.	Acids: HCl, HClO <sub>4</sub> (MgOCl), H <sub>2</sub> PO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub> .
HClO <sub>4</sub> +H <sub>2</sub> SO <sub>4</sub> .	AlCl <sub>3</sub> with halides (Li, Be, Ti, V, Cr, Mn, Fe, Co, Ni).	Nitrous acid.
(CH <sub>3</sub> COOH, H <sub>2</sub> PO <sub>4</sub> ).	Organic complex compounds (benzoyl, acetyl).	Acetic, oxalic, hydrogen ions.
Freshly precipitated HgSO <sub>4</sub> .	Peroxides.	Mg phosphate.
Al <sub>2</sub> O <sub>3</sub> +HgO+H <sub>2</sub> PO <sub>4</sub> .	Surface active substances: silica gel+anthracite, borax, floridin, clays, florida, diatomaceous, and Japanese acid earths.	Surface active substances: silica gel, kieselguhr, activated silicates, hydrosilicates, bleaching, and Florida earths, acid ton.
Al <sub>2</sub> O <sub>3</sub> +(oxides, selenides of Na, Rb, Cs, K, or Fe, Co, Ni).	ZnCl <sub>2</sub> on pumice.	<i>Cyclization</i>
BiCl <sub>3</sub> (hydrolyzable metal halides).	Al <sub>2</sub> O <sub>3</sub> on porous silica.	AlCl <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> .
<i>Polymerization</i>	Persulfates, O <sub>3</sub> , O <sub>2</sub> , and catalysts giving off oxygen.	Acids: H <sub>2</sub> SO <sub>4</sub> , HCl, H <sub>2</sub> PO <sub>4</sub> .
AlCl <sub>3</sub> , BF <sub>3</sub> .	<i>Isomerization</i>	P <sub>2</sub> O <sub>5</sub> .
ZnCl <sub>2</sub> , MgCl <sub>2</sub> .	AlCl <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> .	Oxides: Mg, Mo, Zn, Th, Cr, PbCrO <sub>4</sub> +ZnSO <sub>4</sub> on MgO.
Acids: H <sub>2</sub> SO <sub>4</sub> (KHSO <sub>4</sub> ), H <sub>2</sub> PO <sub>4</sub> (on kieselguhr, charcoal, silica gel).		

Table 1a. Groups of Elements of the Periodic System Active as Catalysts in a Particular Type of Reaction.

Reaction	Group of Periodic System	Elements	Types of Compounds
Synthesis.	VIII	Fe, Ni, Co.	<i>Oxides.</i>
	I	Ag.	Double salts.
	II	Zn.	Alloys.
	VI	Cr.	
	VII	Mn.	
Decomposition.	VIII	Fe, Ni.	<i>Metals.</i>
	VIII	Pt, Pd, Os, Rh, Ir.	<i>Oxides.</i>
	I	Cu, Au, Ag, Na.	Hydroxides.
	II	Zn, Mg, Ca.	Chlorides.
	III	Al.	Carbides.
	IV	Ti, Th, Sn, Zr.	Carbonates.
	VI	Mo, Cr, W, U.	Melts.
Hydration.			Alloys.
	III	Al.	<i>Oxides.</i>
	IV	Th, Ti, Ce, Si.	Double and complex salts.
	II	Zn, Cd, Hg, Ca, Mg.	<i>Halides.</i>
	I	Ag, Au, Cu.	<i>Metaphosphates.</i>
	VI	Mo, W, Cr.	<i>Melts of chlorides.</i>
	VIII	Fe, Co, Ni.	Carbonyls.
Dehydration.			Oxalates.
	III	Al.	Acetates.
	IV	Si, Th, Ce, Zr, Ti, Pb.	Acids (H <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> PO <sub>4</sub> ).
	VI	W, U.	Dehydrated ton.
	II	Mg, Ca, Zn.	<i>Oxides.</i>
	VIII	Fe, Ni.	Earths.
	VII	Mn.	Silicates, hydrosilicates.
Reduction.			Aluminates.
	VIII	Fe, Ni, Co; Pd, Pt.	Phosphates, metaphosphates.
	II	Mg, Zn, Hg, Cd.	Graphite, coke.
	IV	Sn, Pb, Th, Zr, Si, Ti.	Kaolin, Alundum.
	I	Cu, Ag, Au.	<i>Metals.</i>
	VI	Mo, Cr, W.	<i>Oxides.</i>
	VII	Mn.	Alloys.
Oxidation.			Mixtures.
	VIII	Pt, Rh, Ir, Ru; Ni, Fe, Co.	Metals+oxides.
	V	V, Nb, Ta, Bi.	Hydroxides.
	VI	W, Cr, Mo, U.	Chlorides.
	VII	Mn.	<i>Chromates.</i>
	I	Cu, Li, K, Na, Ag.	Acetates.
	IV	Si, Th, Pb, Sn.	Formates.
			Carbonates.
			Kieselguhr.
			Charcoal.
			Graphite.
			Pumice.
			Silica gel.
			Active alumina.
			Earths.
			<i>Oxides.</i>
			<i>Vanadates.</i>
			<i>Alloys.</i>
			<i>Volatile halides.</i>
			<i>Chromites.</i>
			<i>Molybdates.</i>

Table 1 (Continued).

Reaction	Group of Periodic System	Elements	Types of Compounds
Oxidation (Continued)	II	Zn, Hg, Cd.	Carbonates. Hydroxides. Borates. Carbonyls. Acetates. Stearates. Butyrates.
Hydrogenation.	VIII I VI II	Ni, Fe, Co; Pt, Pd. Cu, Ag. Mo, W. Zn.	Metals (Ni). Alloys of Ni or Cu. Salts (organic and inorganic) on carriers. Mixtures with oxides. Oxides (Mo, W, Zn). Sulfides (Mo, W). Melts (Sn).
Dehydrogenation.	VI VIII V IV I II	Cr, Mo. Pt, Pd, Re, Ni. V. Zr, Ti, Si, Th, Ce, Pb. Cu, Ag. Mg, Hg, Be, Ca, Sr, Ba, Zn.	Metals (Pt, Pd). Oxides. Mixture of difficultly and readily reducible oxides. Mixtures. Salts. Molybdates. Tellurides. Selenides. Sulfides. Phosphides. Alloys.
Chlorination.	III VII V IV II I VIII	Al. I. Sb, Bi. Sn, Si. Zn, Hg, Mg. Cu, Na. Fe.	Adsorbents. Impregnated melts of chlorides. Halides. Double salts. Oxides.
Dechlorination.	II I VIII	Ba, Ca, Zn, Mg. Na, Cu. Fe.	Chlorides. Oxides. Metals.
Bromination.	II III IV VII	Be, Mg, Zn, Cd. Al. Sb. I.	Metal bromides. Organic bromides with active adsorbents (charcoal, Si or Al gel).
Fluorination.	II V	Hg. Sb.	Halides. Chlorides, or fluorides on active charcoal. Oxides.
Iodination.	III VII	B, Al. I, Cl.	Fluorides. Chloride. Oxide. Acetate (oxalate).
Nitrogenation.	II I	Ca. K.	Charcoal, silica gel. Acid mixture ( $H_2SO_4 + HNO_3$ ). Chlorides. Cyanide. Double salts ( $KOH \cdot K_2CO_3$ ).
Denitrogenation.	I	Cu.	Metal (powder). Oxide.
Sulfurization.	II I V VII VIII	Hg, Ca, Ba, Mg. Cu, Ag, Na. V. Mn. Ni, Fe.	Sulfates. Oxides. Sulfides.
Desulfurization.	VI VIII I	Mo, Cr, W. Ni, Fe, Co. Na, Cu.	Porous active substances: charcoal, kieselguhr, asbestos, bauxite, earths, etc. Oxides. Sulfides. Chlorides. Molybdates. Aluminates. Chromites (used on carriers).



Table 1 (Continued).

Reaction	Group of Periodic System	Elements	Types of Compounds
Alkylation.	III IV II V	Al, B. Zr. Zn. P.	Chlorides (anhydrous). Fluorides. Bromides. Acids ( $H_2SO_4$ , $H_3PO_4$ ). Activated silicates. Earth, clay, kaolin. Activators: $H_2S$ , $HCl$ , $HBr$ , $HI$ , $HCN$ , $H_2O$ .
Destructive alkylation.	III	Al.	Chlorides. Acids ( $H_3PO_4$ ).
Condensation.	III II IV V VI I VIII	Al, B. Ca, Ba, Sr, Mg, Zn. Sn, Zr, Hg, Th, Si. V, Bi. U. Cu, Ag, Li. Fe.	Basic oxides. Chlorides. Surface-active substances. Acids ( $H_3PO_4$ , $H_2SO_4 + HClO_4$ , $CH_3COOH$ ). $P_2O_5$ . $P_2O_3$ . Mixtures of oxides and selenides. Phosphates (Ag).
Polymerization.	III II	Al, B. Zn, Mg, Be.	Chlorides. Acids ( $H_2SO_4$ , $H_3PO_4$ , $HClO_4$ (molybdic acid)). Surface-active substances. Complex organic compounds. Double salts: $AlCl_3$ with halides (8th Group, Fe, Co, Ni); (2nd Group, Be); (1st Group, Li); (5th Group, V); (6th Group, Cr). Persulfates. $O_3$ , $O_2$ . Catalysts giving off $O_2$ .
Isomerization.	III IV II	Al. Zr. Mg.	Chlorides. Acids ( $H_3PO_4$ , $H_2PO_4$ , $HClO_4$ , $HCl$ ). Surface-active substances. Oxides (Al).
Cyclization.	III II IV VI	Al. Zn, Mg. Th, Pb. Mo, Cr.	Chlorides. Oxides. Acids ( $H_2SO_4$ , $HCl$ , $H_3PO_4$ ). $P_2O_5$ .

Table 2. Groups of Catalysts for Various Reactions of Single Compounds.

a. Ammonia.		
Synthesis	Decomposition	Oxidation
Fe (thermo-ionic emission from Fe-alkali contact).	Fe: activated.	Pt (glowed, gauze, grain).
Pyrophoric Fe.	colloidal $Fe(OH)_3$ .	Pt plated on Cu.
Fe (oxides, carbonate, peroxide, oxalate, carbide).	Fe ions.	Pt plated on Ag.
Complex salts of Fe: $AlFe(NH)_4$ .	Mineral water with high content of $Fe^{++}$ and $Mn^{++}$ .	Pt plated on brass.
$K_2Fe(CN)_6 + KCl$ .	Fe (ferrous and ferric salts, nitride, azide, sulfate):	Pt plated on quartz.
Mixtures:	Fe (bipyridine) $_2$ .	Pt plated on fibers.
Fe cyanide + Ti magnetite.	Fe (phenanthroline) $_2$ .	Pt plated on pozzuolan earth.
Fe + As, B, P.	Mixtures:	Pt-Ag alloy.
Fe + Mo.	$Fe(OH)_2 + Cu(OH)_2$ .	Pt-Ag-Rh alloy.
Fe + Al.	Fe + $Al_2O_3$ or MgO (on Fe wire).	Pt-Ir alloy.
Fe + $ZrO_2$ .	Fe + $Al_2O_3 + K_2O$ .	Pt-Ru alloy.
Fe + $Al_2O_3 (K_2O)$ .	$FeSO_4 + Na_2WO_4$ .	Pt-Rh alloy.
Fe + Mo + $Al_2O_3$ .		Pt-W alloy.
Pt, Rh, Os.	Au (thin layer), colloidal.	Pt + Rh + W alloy.
Os + K (vapor).	$Ag_2O$ , $Ag_3O_2$ .	Pt + $WO_3$ (Mo, Nb, or Cr oxides).
Pt-asbestos.	Ag colloidal.	Pt + $Fe_2O_3$ (containing Bi or Cu).
Rh-pumice.	Ag powder (thin layer on glass).	
Pt-chamotte.	Pt (black, colloidal, illuminated with x-rays).	Cr, Cr steel.
Mn (oxide, carbonate).	Os, Rh, Pd.	Chromate.
Complex salts:		Cr on pozzuolan earth.
$K_2Mn(CN)_6$ .	Cu.	Cr on Celite sticks.
$Ba_2Mn(CN)_6$ .	Cu (oxide, sulfate, hydroxide, acetate).	$Cr_2O_3$ on silica gel + Al.
$MnO_2 + Fe_2O_3$ .		Cr silicate + alkali.
Ni + Mo.		Alkalies and alkaline earths on polyzeolites, Ca + Sn on $SiO_2$ .
		Cu (brass gauze).
		$V_2O_5$ .

Table 2 (Continued).

*Synthesis* (Continued)Al<sub>2</sub>O<sub>3</sub> + alkalis.*Decomposition* (Continued)W (wire, powder) light of a W lamp.  
Na<sub>2</sub>WO<sub>4</sub>.CrO<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>.  
Cr(CH<sub>3</sub>COO)<sub>3</sub>, MnSO<sub>4</sub>.  
K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + (CoCl<sub>2</sub>, Mn salt).Active charcoal.  
Sugar charcoal.  
Blood charcoal.  
Charcoal + MnO<sub>2</sub>(PbO<sub>2</sub>).  
Catalase.  
Haemine.I', CdI<sub>2</sub>, CdI<sub>3</sub>.  
Cl acid-chlorine system.*Oxidation* (Continued)

Os or Ni on fibers.

## b. Methane.

*Synthesis*Ni, NiO.  
Ni + Th (on pumice).  
Ni + Al<sub>2</sub>O<sub>3</sub>.  
Ni + Mn.  
Ni-Mn-Al-Fe.  
Ni-Mn-Al-Mg (on kieselguhr).  
Ni-ThO<sub>2</sub> + CeO<sub>2</sub>.  
NiO + Fe<sub>2</sub>O<sub>3</sub>.Fe, Fe<sub>2</sub>O<sub>3</sub>.  
Fe-Cu.  
Fe + alkali.  
Fe containing S activated by alkali.Co, CoO.  
Cu + Zn.  
Co + alkali.  
Co + Fe-Cr<sub>2</sub>O<sub>3</sub>.  
CoO + Fe<sub>2</sub>O<sub>3</sub>.  
Co(NO<sub>3</sub>)<sub>2</sub> + KMnO<sub>4</sub>.*Decomposition*Fe, Co, Ni on porcelain, kaolin, MgO, Al<sub>2</sub>O<sub>3</sub>, kieselguhr.  
Melted Mg, Ni, Ag, Cu.  
Fe, Co, Ni oxides + Ni vanadate or Co uranate or Fe tungstate.  
V or Mo on kieselguhr.  
Pt wire.  
Zr ore.*Oxidation*Ni or Co (wire gauze, filings).  
Ni or Co on fireproof material.  
Ni or Co on ton pieces.  
Ni or Co on MgO (1 g. mol MgO : 1 g. atom Ni).  
Ni or Co on charcoal.  
Ni or Co on alumina.  
Ni or Co on silica gel.  
Ni or Co on kaolin.  
Ni or Co on artificial Al silicate.  
Ni or Co on unburned Al compounds.  
Ni or Co mixtures.  
Ni + CeO<sub>2</sub> (ThO<sub>2</sub>).  
Ni(Co) + difficultly reducible oxides.  
NiO + Co<sub>2</sub>O<sub>3</sub>.  
Ni + Al<sub>2</sub>O<sub>3</sub> (ZrO<sub>2</sub>, ThO<sub>2</sub>, CaO, CdO, ZnO).  
Ni + Cr<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub> on kaolin.  
Ni(OH)<sub>2</sub> · Al(OH)<sub>3</sub>.Fe, Fe<sub>2</sub>O<sub>3</sub>.  
Fe (oxide, phosphate).  
Fe<sub>2</sub>O<sub>3</sub> + Cr<sub>2</sub>O<sub>3</sub> (on pumice, asbestos, or quartz).  
Fe + difficultly reducible oxides.  
Fe-Cr alloy.  
Fe<sub>2</sub>O<sub>3</sub>-Cu.  
Fe on Al silicate, bauxite, kaolin.  
Fe on charcoal.  
Fe + Cr(V) oxide.Cu, CuO.  
Cu-CeO<sub>2</sub>.  
Cu-Cr<sub>2</sub>O<sub>3</sub>.  
Cu-CuO.  
Cu-UO<sub>2</sub>.  
Cu-MoO<sub>3</sub>.  
Cu-Al<sub>2</sub>O<sub>3</sub>.  
Cu-V<sub>2</sub>O<sub>5</sub>-CeO<sub>2</sub>.  
CuO + Cr<sub>2</sub>O<sub>3</sub>.  
CuO on silicic acid gel.Pt (wire).  
Pt on silicic acid gel.Sn or Al phosphate.  
Ag.  
Boric acid on clay.  
Lime.  
Brick, coke.

## c. Carbon Monoxide.

*Decomposition*Ni (powder).  
Ni (oxide, carbide).  
Ni + oxides or hydroxides of Mn, V, Cr, U, Zn, Al, Cd, or Cu, also their silicates, molybdates, tungstates, chromates.  
NiO + Ni vanadate.  
NiO + Co uranate.*Decomposition* (Continued)NiO + Fe tungstate.  
Ni on porcelain.  
Ni on kaolin.  
Fe (from Fe glance by reduction).  
Fe (oxides, carbides).  
Fe + C (mixture).

Table 2 (Continued).

<i>Decomposition (Continued)</i>		<i>Hydrogenation</i>	
Mo carbide.		Fe (powder, filings, etched surface).	
ZnO.		Fe (hydroxide, nitrate, oxides, acetate).	
	<i>Oxidation</i>	Fe-Cu + K <sub>2</sub> CO <sub>3</sub> .	
Mn.		Fe + Th or Cd.	
MnO <sub>2</sub> , Mn <sub>2</sub> O <sub>3</sub> , MnO <sub>4</sub> finely dispersed.		Fe(OH) <sub>2</sub> + Al(OH) <sub>3</sub> .	
MnO <sub>2</sub> + NiO.		Zn-Cu-Cr.	
MnO <sub>2</sub> + CuO (CuO <sub>2</sub> ).		Zn-Cu.	
		Ni-Cu.	
MnO <sub>2</sub> + CoO.		NiO + KOH.	
MnO <sub>2</sub> + Ag <sub>2</sub> O.		2CO + 4H <sub>2</sub> → 2CH <sub>4</sub> O <sub>2</sub> .	
Hopcalite (dehydrated at 180°):		Ni, NiO, NiO + Fe <sub>2</sub> O <sub>3</sub> .	
50% MnO <sub>2</sub> .		Ni + Th, Ni + Mn.	
30% CuO.		Ni + Al <sub>2</sub> O <sub>3</sub> , Ni + Mn + Al + Mg.	
15% Co <sub>2</sub> O <sub>3</sub> .		Ni + ThO <sub>2</sub> + CeO <sub>2</sub> .	
5% Ag <sub>2</sub> O.			
Mn <sup>III</sup> (from a mixture of bi and ter valent Mn).		Fe, Fe + Cu.	
Mn in Mo steels.		Fe, Fe + Alkali.	
		Fe, Fe oxide + Ni oxide.	
Fe (cast iron) (glowed at 700°).		Co, CoO, CoO + Fe <sub>2</sub> O <sub>3</sub> .	
Colloidal Fe.		Co + Zn, Co(NO <sub>2</sub> ) <sub>2</sub> + KMnO <sub>4</sub> .	
Fe (oxides, hydroxide, chromite, sulfate, carbonate).		Co + Alkali.	
Fe <sub>2</sub> O <sub>3</sub> · MgO.		Co + Fe + Cr <sub>2</sub> O <sub>3</sub> .	
Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> + K <sub>2</sub> O.		CO + 2H <sub>2</sub> → CH <sub>3</sub> OH.	
FeSO <sub>4</sub> + NH <sub>3</sub> + chromic acid.		Zn (chromate, carbonate, sulfide, nitrate, hydroxide).	
Fe containing Cr <sub>2</sub> O <sub>3</sub> on active charcoal.		Zn-Cr, ZnO + CuO.	
Fe(OH) <sub>3</sub> + Na <sub>2</sub> CO <sub>3</sub> .		Zn-Cu, ZnO + V <sub>2</sub> O <sub>5</sub> .	
FeCO <sub>3</sub> + K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (0.7%) on MgO.		Zn-Cu-Cr(Al), ZnO + WO <sub>3</sub> .	
		Zn + Cr <sub>2</sub> O <sub>3</sub> , ZnO + Cr <sub>2</sub> O <sub>3</sub> .	
		ZnO + Mo <sub>2</sub> O <sub>3</sub> .	
		ZnO + UO <sub>2</sub> .	
		ZnO + Cr <sub>2</sub> O <sub>3</sub> + Li.	
		ZnO + Cr <sub>2</sub> O <sub>3</sub> + CuNO <sub>2</sub> .	
		ZnO + CuO + Cr <sub>2</sub> O <sub>3</sub> .	
		ZnHCO <sub>3</sub> + H <sub>2</sub> CrO <sub>4</sub> .	
		Ni.	
		Ni (oxide, hydroxide, nitrate, oxalate, formate).	
		Ni on kieselguhr.	
		Cu.	
		Cu (oxide, chromite, carbonyl, hydroxide).	
		Cu + Cu <sub>2</sub> O, Cu-Zn alloy.	
		Cu + CeF <sub>3</sub> .	
		CuO + MnO.	
		CuO + MnO + CoS <sub>2</sub> .	
		Sn phosphate.	
		Cr-Mn nitrate.	

## d. Methanol.

<i>Synthesis</i>	<i>Synthesis (Continued)</i>	<i>Dehydration</i>
Zn.	Ni, NiO.	Al <sub>2</sub> O <sub>3</sub> .
Zn (oxide, chromate, carbonate, sulfide, nitrate, hydroxide).	Ni(OH) <sub>2</sub> , Ni(NO <sub>2</sub> ) <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> on pumice, glowed kaolin (water content, 1%).
Zn-Cr (75% : 25%).	Ni (oxalate, formate) on kieselguhr.	Glassy Al <sub>2</sub> O <sub>3</sub> activated with small amounts of oxides.
Zn-Cr-Cu.		CeO <sub>2</sub> on pumice.
Zn-Cu.	<i>Decomposition</i>	Silicic acid gel.
Zn-Cu-Al.	Zn, ZnO.	Silica gel + ThO <sub>2</sub> .
ZnO-CuO.	Zn-Cu.	W <sub>2</sub> O <sub>5</sub> , WO <sub>3</sub> (90%).
ZnO-Cr <sub>2</sub> O <sub>3</sub> + Li.	Zn-Cr <sub>2</sub> O <sub>3</sub> .	
ZnO-Cr <sub>2</sub> O <sub>3</sub> + CuNO <sub>2</sub> .	ZnS + CdS.	
ZnO + Mo <sub>2</sub> O <sub>3</sub> .	MoS <sub>2</sub> , CuS.	
ZnO + UO <sub>2</sub> .	Sb <sub>2</sub> S <sub>3</sub> .	<i>Dehydrogenation</i>
ZnO + V <sub>2</sub> O <sub>5</sub> .	Ni + Cu.	Cu.
ZnO + WO <sub>3</sub> .	Ni aerosol.	Cu + Ag.
ZnO + Cr <sub>2</sub> O <sub>3</sub> .		Cu + Ce.
ZnO + CuO + Cr <sub>2</sub> O <sub>3</sub> .		Cu + Zr.
ZnHCO <sub>3</sub> + H <sub>2</sub> CrO <sub>4</sub> .		Cu-ZrO <sub>2</sub> .
		Cu + CeO <sub>2</sub> .
Cu, CuO.	<i>Oxides.</i>	Cu (Ag, Co) on silica gel.
Cu(OH) <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Cu + H <sub>2</sub> PO <sub>4</sub> (NaHPO <sub>4</sub> or Ba <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ).
Cu + Cu <sub>2</sub> O.	Cr <sub>2</sub> O <sub>3</sub> .	Cu + oxides of (Cr, Mn, Mg).
CuO + MnO.	Co <sub>2</sub> O <sub>3</sub> .	Cu tube with brass.
CuO-MnO-CoS <sub>2</sub> .	<i>Metals of the Pt group.</i>	
Cu-Zn alloy.	Ag-wool.	
	Re finely dispersed.	

Table 2 (Continued).

*Dehydrogenation (Continued)*

Al<sub>2</sub>O<sub>3</sub>.  
Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>.  
Al<sub>2</sub>O<sub>3</sub> + Cr<sub>2</sub>O<sub>3</sub>.  
Al<sub>2</sub>O<sub>3</sub> + SnO.  
Al<sub>2</sub>O<sub>3</sub> + ZnO.  
Al<sub>2</sub>O<sub>3</sub> + NiO.  
V<sub>2</sub>O<sub>5</sub>.  
UO<sub>2</sub>.  
MoO<sub>3</sub>.

*Oxidation*

Cu (gauze).  
Cu-Pt.  
Cu-Th.  
Cu-Ce.  
Cu-ThO<sub>2</sub>.  
Cu plated with Ag.  
Cu on asbestos.

*Oxidation (Continued)*

Ag on pumice, asbestos, or porcelain.  
Mo and Fe oxides;  
mixtures of heavy metal oxides  
and base exchanging bodies.

*Chlorination*

Active charcoal.  
Silica gel.  
Al<sub>2</sub>O<sub>3</sub>.

*Condensation*

Condensation with H<sub>2</sub>S:  
Oxides: ThO<sub>2</sub> > Al<sub>2</sub>O<sub>3</sub>  
bauxite, active charcoal.

*Condensation (Continued)*

Condensation with nitro compounds:  
ThO<sub>2</sub>-asbestos.  
ZnO-silica gel.  
ZnO : Al<sub>2</sub>O<sub>3</sub> : silica gel.  
Al<sub>2</sub>O<sub>3</sub>-silica gel.  
Condensation with olefins:  
Al<sub>2</sub>O<sub>3</sub>.  
Al(OH)<sub>3</sub> + tungstic acid.  
H<sub>3</sub>PO<sub>4</sub> + silicic acid.  
H<sub>3</sub>PO<sub>4</sub> + kieselguhr.  
Cr or Ce metaphosphate.  
Ce salt of P-W acid + 10% H<sub>3</sub>PO<sub>4</sub>.  
Condensation with ketones:  
Al<sub>2</sub>O<sub>3</sub> impregnated with Cu formate and MoO<sub>3</sub>.

## e. Benzene.

*Synthesis*

Ni, Fe, Co.  
Cu (powder).  
Alloy skeletons.  
Mixtures:  
NiO + Al<sub>2</sub>O<sub>3</sub> + MnO.  
Ni + ThO<sub>2</sub>(UO<sub>2</sub>).  
Ni oxalate + UO<sub>2</sub>.

*Oxidation*

V<sub>2</sub>O<sub>5</sub>.  
V<sub>2</sub>O<sub>5</sub> on pumice.  
V<sub>2</sub>O<sub>5</sub> on asbestos.  
Mixture:  
V<sub>2</sub>O<sub>5</sub> + MoO<sub>3</sub> + Co<sub>2</sub>O<sub>3</sub>.  
Vanadic acid on pumice, graphite, granulated Al or Si gel.  
NH<sub>4</sub> metavanadate in methylbenzyl.  
NH<sub>4</sub>OH.  
Oxides of U, Mo, W, Nb, Ta, Cr, Mn.  
Silicic acid gel impregnated with sulfates, phosphates, carbonates, arsenates of alkalies and alkaline earths.  
Fe, Co, Ni, Cu, or Al oxides on active silicates or nonexchangeable bases.

*Chlorination*

Halides of heavy metals.  
ZnCl<sub>2</sub>, FeCl<sub>3</sub>.  
FeBr<sub>3</sub>, FeI<sub>3</sub>.

*Chlorination (Continued)*

Iodine with Fe very active, surpassing the activity of chlorine carriers (1% Fe + 1% I).  
Melts of metal chlorides, such as eutectic mixtures of AlCl<sub>3</sub>, NaCl, and FeCl<sub>3</sub>.  
SbCl<sub>3</sub> + S + Fe(Pb).  
HCl-methyl alcohol suspended in the hydrocarbon mixture di-, tri-, and poly-hydrochlorides, forming amines with CH<sub>3</sub>O and butanol.

*Alkylation*

AlCl<sub>3</sub> (AlBr<sub>3</sub>).  
BF<sub>3</sub>, ZrCl<sub>4</sub>.  
TaCl<sub>5</sub>, FeCl<sub>3</sub> (anhydrous).  
Acids:  
H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>.  
P<sub>2</sub>O<sub>5</sub> with activators: HCl, HBr, HCN, H<sub>2</sub>O, H<sub>2</sub>S, HF.

*Condensation*

H<sub>3</sub>PO<sub>4</sub>.  
P<sub>2</sub>O<sub>5</sub>.  
P<sub>2</sub>O<sub>5</sub>.  
Al (alkali-free).  
Al (powder) + HgCl<sub>2</sub>.  
Mg silicate.  
Ni.  
Heated carbon.  
Graphite.

## f. Naphthalene.

*Oxidation*

Vanadium compounds.  
V<sub>2</sub>O<sub>5</sub>.  
V<sub>2</sub>O<sub>5</sub> on pumice.  
VOCl<sub>3</sub>.  
Vanadates (W, Bi, Sn).  
Vanadic acid on carriers (kieselguhr, bone charcoal, silica gel, melted Al<sub>2</sub>O<sub>3</sub>).  
Vanadium containers covered with Ni or Al.  
Mixtures:  
V<sub>2</sub>O<sub>5</sub> (18 parts dissolved in conc. NaOH or KOH) + 42 parts K<sub>2</sub>SiO<sub>3</sub> + 70 parts zeolite.  
Oxides (Mo, Ti, Cd, Zn, Al).  
Al<sub>2</sub>O<sub>3</sub> on carbides of the 4th group of elements.  
Bi better than Hg (Hg in strong H<sub>2</sub>SO<sub>4</sub>).

*Hydrogenation*

Ni (from formate, hydroxide, nitrate).  
Ni (splinters, Raney's).  
Ni-Co.  
Ni + Cu.  
Ni + Cr.  
Ni-Hg.  
Ni-Th.  
Ni-Mo.  
Ni + formates (Cu, Al, Fe).  
37% Ni + 63% Na aluminate.  
20% Ni on silica gel (kaolin).  
Ni on kieselguhr, powdered pumice.  
Ni + NaK · NaK<sub>2</sub> (alloys).

*Hydrogenation (Continued)*

NiO on ton pieces (kieselguhr).  
Mo.  
(NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> on active charcoal.  
MoO<sub>3</sub> + brown charcoal.  
MoS<sub>2</sub> (2%) + S (2.5-5%).  
MoS<sub>2</sub> on Al<sub>2</sub>O<sub>3</sub>.  
Mo + W + difficultly reducible oxides.  
WO<sub>3</sub> + S.  
Pt black on (Al<sub>2</sub>O<sub>3</sub>, BaSO<sub>4</sub>).  
PtO (Adams).  
Pd black on BaSO<sub>4</sub>.  
Fe (iodide, oxide).  
Fe (Co, Ni), especially their oxides (Fe<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub> + small amount of alkali).  
Na, NH<sub>3</sub>, NaH, K, Na on kieselguhr.

*Dehydrogenation of Hydronaphthalene*

Pt.  
Pd.  
Pt on charcoal (asbestos).  
Os.  
Oxides (Cr, Cu).

*Condensation*

BF<sub>3</sub>.  
Chlorides (Al, Fe, Cr, Ti, Sn, Sb, Zn, Mg, Ca).  
Oxides (Al<sub>2</sub>O<sub>3</sub>).  
Al<sub>2</sub>O<sub>3</sub> covered with anthracite.  
Al<sub>2</sub>O<sub>3</sub> + dehydrogenating catalysts.

Table 2 (Continued).

Condensation (Continued)	Condensation (Continued)
Anhydrides (phosphoric, acetic). Organic bases. Surface active substances: earths (japanese acid, bleaching).	Silicic acid, aluminum gels. Acids (mineral, oxalic, silicic). Na methyrate. Ag phosphate (dissolved in H <sub>3</sub> PO <sub>4</sub> ).
Table 3. Groups of Catalysts Typical of Reactions of Saturated and Unsaturated Hydrocarbons, Aromatics and Terpenes.	
a. Paraffins.	
Oxidation	Dehydrogenation of Cycloparaffins
Cu. Cu (sulfate, oxide). CuO + NiO + Mn salts. Cu + V <sub>2</sub> O <sub>5</sub> . CuO + 2% CoO (Ni or Mn oxide). Mn (resinate, stearate, phosphate, borate). Na or KMnO <sub>4</sub> . Metallic soaps. Metal enolates. Organic compounds of alkaline earth metals. Hetero complexes of Mo, W, U and Co. Oxides of high melting electronegative metals with low atomic volume and atomic weight above 40. Colloidal catalyst. Nitrogen oxides. Pumice, glass, porcelain.	Pt, Pd. Pt, Pd impregnated on carriers (active charcoal, asbestos). Ni on Al <sub>2</sub> O <sub>3</sub> . Silica gel or alumina covered with anthracite. Molybdates or tungstates of heavy metals (Cu, Ag, Fe, Ni) on silica gel or active charcoal. Oxides (Al, Cr, Ti) on charcoal. Hydroxides mutually precipitated. Mg(OH) <sub>2</sub> + Cu(OH) <sub>2</sub> = 4 : 1.
Dehydrogenation	Alkylation
Oxides (Cr, Mo, Al, V, W, Mn, Zn). Mixtures of oxides: 70% Cr <sub>2</sub> O <sub>3</sub> + 30% Zn. 25% Cr <sub>2</sub> O <sub>3</sub> + 40% Al <sub>2</sub> O <sub>3</sub> . Cr <sub>2</sub> O <sub>3</sub> + Bi <sub>2</sub> O <sub>3</sub> . Cr <sub>2</sub> O <sub>3</sub> + difficultly reducible oxides. 4% Cr <sub>2</sub> O <sub>3</sub> + 96% Al <sub>2</sub> O <sub>3</sub> + 1% graphite + 2% B(OH) <sub>3</sub> . 5% Cr <sub>2</sub> O <sub>3</sub> + 90% MgO + 5% ZnO. CeO <sub>2</sub> + ZnO. VO <sub>3</sub> (TaO <sub>3</sub> ) on Al <sub>2</sub> O <sub>3</sub> . Nd compound on Al <sub>2</sub> O <sub>3</sub> . NiO (CuO, CoO, ZnO) + CaCO <sub>3</sub> on pumice. 35 g. Al <sub>2</sub> O <sub>3</sub> + 25 g. Cr <sub>2</sub> O <sub>3</sub> on white ware. Cr <sub>2</sub> O <sub>3</sub> (large amount) on Al <sub>2</sub> O <sub>3</sub> . 30% Pt on active charcoal. CuO : pumice : coal (1 : 1 : 1). Surface active substances: active charcoal, alumina, silicic acid, clay (Montmorillonite type), fuller's earth charged with Co or Fe or a mixture of NH <sub>4</sub> molybdate, cobalt nitrate and H <sub>3</sub> PO <sub>4</sub> .	Metal chlorides. Chlorides (Al, Zr, Zn) in the presence of HCl. BF <sub>3</sub> . HF + BF <sub>3</sub> . Finely dispersed Ni.
	Condensation
	Chlorides (Al, Zr, Mg, Zn). BF <sub>3</sub> . Basic oxides (Al, U, Th) mixed with Cu, Ag, Ni and/or Cr not exceeding 10%. Basic oxides (Ca, Ba, Sr, Mg, Li). Oxidation catalysts together with bleaching earth, silica, porous active charcoal.
	Isomerization
	Halides (Al, Zn, Sn, Fe, Zr, Be, Nb, Ta). AlCl <sub>3</sub> (20 parts) + HCl (2 parts). AlCl <sub>3</sub> and propyl chloride. AlCl <sub>3</sub> on charcoal. AlBr <sub>3</sub> . Hydrogen halide + small amount of B. Pt on active charcoal.
b. Olefins (Ethylene).	
Hydration	Oxidation (Continued)
Oxides (Al, Th, W, Si, Ti, Zr, Cr), alkalies and alkaline earths. Carbonyls (V, W, Mo). Chlorides (Ca, Zn, Mg) or bisulfates. Metaphosphates (alkalies and alkaline earths). Halides (Al, Cd, Zn). Complex salts (Fe, Co, Ce). Oxalates (Au, Ag, Cu, Fe, Ni, Co, Cr). Ag <sub>2</sub> SO <sub>4</sub> (Ag <sub>2</sub> S) + 70% H <sub>2</sub> SO <sub>4</sub> on charcoal. Alkaline earths on silica gel. Mn on silica gel. CuO + WO <sub>3</sub> on active charcoal. BF <sub>3</sub> , BF <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> . Acids (H <sub>2</sub> SO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub> , acetic or oxalic).	Mn) or (Co, Ni, Zn, Th, Ce), also on a carrier (active charcoal, silica gel). Ag-Au, Ag-other metals. Pd, Pt (black), Os on silica gel. Oxides (Sb, Pb, Bi, V, W, Cr, Ni, Sn, As, Mo on silica gel). Volatile halide compounds (HCl, HI, HBr, CH <sub>3</sub> Cl, CCl <sub>4</sub> , NH <sub>4</sub> Cl) on carriers (pumice, silica gel, coke). Alkalies, KMnO <sub>4</sub> , KClO <sub>4</sub> on pumice. Acids (boric, phosphoric, pervanadic, heteropolyacids, tungsten-arsenic acid on alumina).
Reduction	Hydrogenation
Ni containing NaOH on silica gel. Ni mixed with BaO. Oxides (Pt, Cr).	Ni (finely dispersed, wire, ribbon). Ni (chromite, carbonate, sulfate, formate) reduced. Ni-Pd (on alumina, pumice). Ni-Cu (alloy) (75% Ni). Ni-Mo. Ni-Al <sub>2</sub> O <sub>3</sub> -ThO <sub>2</sub> . Ni : Al <sub>2</sub> O <sub>3</sub> (100 : 2.5) (alloy). Pt, Pd, Rh (black, colloidal). Pt, Pd (chlorides) + gum arabic. Pt black (Willstätter).
Oxidation	Hydrogenation (Continued)
Ag (finely dispersed). Ag (oxide, acetate, formate, oxalate) mixed with (Cu, Au, Fe,	Rh, Au on carriers (charcoal, asbestos, pumice, active silica). Cu (poisoned with CO). Cu on kieselguhr. Cu-Ag (alloy). Cu-Zn chromate. Cu (Zr, Ce, Co) + Al or Ni (alloy). Cu + Mg (hydroxide) (1 : 4). Cu Chromite + Cr <sub>2</sub> O <sub>3</sub> . Zn. Zn (oxide, chromite). Zn + Cd. Zn + Co <sub>2</sub> O <sub>3</sub> . ZnO + MoO <sub>3</sub> . ZnO + Al <sub>2</sub> O <sub>3</sub> . Fe (filings). Fe + K <sub>2</sub> O (1.6%) or Al <sub>2</sub> O <sub>3</sub> (1.3%).
	Halogenation
	(1) Chlorination: Active adsorbents: charcoal, diatomite, dehydrated bauxite, asbestos, kieselguhr, silica gel used alone or as carriers. Chlorides (Al, Mg, Ba, Bi, Zn, Fe, Sb). Double compounds (AlCl <sub>3</sub> + FeCl <sub>3</sub> ) (AlCl <sub>3</sub> + Zn). Acids (HCl, H <sub>3</sub> PO <sub>4</sub> ) on carriers (charcoal, kieselguhr, silica gel).

Table 3 (Continued).

**Halogenation (Continued)**

I<sub>2</sub>.  
Zn halide activated by mono- or polyvalent metals on charcoal, kieselguhr, silica gel.  
SbCl<sub>3</sub> (SbCl<sub>5</sub>) on charcoal.  
BiCl<sub>3</sub> on asbestos.

**(2) Bromination:**  
*HBr (in statu nascendi).*

Metal bromides mixed with active charcoal, silica, or alumina gel.

Organic bromides (C<sub>2</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>).

*HBr, SbBr<sub>3</sub>.*

Polar liquids (H<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>COOH).

**Condensation****(1) with H<sub>2</sub>S:**

Al (oxide, chloride).  
Chlorides (Zn, Fe).  
BF<sub>3</sub>.  
Hydrosilicates (bleaching earth).  
Silica gel.  
Bentonite.  
Kieselguhr + Ni.  
Charcoal + H<sub>2</sub>PO<sub>4</sub>.

**(2) with aromatics:**

Chlorides (Al, Zn).  
Highly porous silicates (kaolin).  
Hydrosilicates.

**Hydration**

Hg salt solutions.  
Hg or HgO in H<sub>2</sub>SO<sub>4</sub>.  
HgO + Fe<sub>2</sub>O<sub>3</sub> (suboxide of Hg oxidized to the oxide by reducing Fe<sub>2</sub>O<sub>3</sub> to the suboxide of Fe).  
HgSO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> in dilute methanol or acetic acid.  
HgO on active charcoal.  
Salts of Fe, Zn, Cr, Mo, W.  
Mixtures: Fe<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub>; Fe salts with Cr or Si acids; Fe<sub>2</sub>O<sub>3</sub> + hydrates of Al, Hg, or Si; Zn acetate + Mn acetate on charcoal; ThO<sub>2</sub> and double salts of Th and alkalies or alkaline earths, K<sub>2</sub>Th(CO<sub>3</sub>)<sub>2</sub>; Fe ore.

**Oxidation**

Hg and its compounds in acid solutions.  
Hg salt in free acid.  
HgO or HgSO<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub>.  
Hg<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub> in H<sub>3</sub>PO<sub>4</sub>.  
Hg<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> in aromatic sulfonic acids.  
Hg in Fe sulfate solution.  
Metallic Hg added to dilute acids replaced by oxidation agents.

**Zn mixtures.**

ZnO + (Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, MnO, or ThO<sub>2</sub>).

ZnO : MnO = 4 : 1.

Zn(Cd) basic compounds mixed with charcoal.

Zn acetate + Mn acetate.  
Double salt: 2ZnO · V<sub>2</sub>O<sub>5</sub>.

Vanadates (Cd, Cr, Mo).

Nitrogen oxides.

Cd(Cr) + ThO<sub>2</sub>.

H<sub>2</sub>PO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub> containing Zn, Cd, or Ag on active charcoal.

**Hydrogenation**

Pt black.

**Condensation (Continued)**

Activated silicates (treated with acids).

AlCl<sub>3</sub> or ZnCl<sub>2</sub> on bentonite, fuller's earth.

Acids (H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, HClO<sub>4</sub>, CH<sub>3</sub>COOH) on (kieselguhr, silicic acid).

P<sub>2</sub>O<sub>5</sub> (dispersed on fuller's earth, silica gel).

BF<sub>3</sub>.

**Polymerization**

Chlorides (Al, Zn, Sn, Ta, Zr).

NaAlCl<sub>4</sub>.

Fluorides (B, Al).

BF<sub>3</sub> + (HI, HF, Ni, EtCl).

Al (silicate, bromide).

Acids: H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> (liquid, solid), H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>AsO<sub>4</sub>, molybdic acid, H<sub>2</sub>TiO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub> (activated by AlCl<sub>3</sub>, PCl<sub>3</sub>, PCl<sub>5</sub>, NiO, NiCl<sub>2</sub>).

Solid calcined H<sub>3</sub>PO<sub>4</sub>.

H<sub>2</sub>PO<sub>4</sub> on active substances: chamotte, calcined kieselguhr, charcoal, bleaching earths.

Pyrophosphoric acid better than H<sub>2</sub>PO<sub>4</sub>.

Phosphates (Cd, minerals).

Metaphosphate (Ce).

P<sub>2</sub>O<sub>5</sub> (on soot mass).

Organo-metallic compounds (Hg ethyl, tetraethyl Pb).

Oxides (Al<sub>2</sub>O<sub>3</sub>).

Benzoyl peroxide.

**Polymerization (Continued)**

Ni (finely dispersed).

Co on charcoal.

Co + Ag.

Co-Cu.

Co + Ag + U<sub>3</sub>O<sub>8</sub> + ThO<sub>2</sub>.

Fe-Cu.

Hg (ultraviolet light).

Heavy metal sulfides.

Active adsorbents: floridin, borax, silica gel (covered with anthracite).

**Hydropolymerization**

Polymerization catalysts: AlCl<sub>3</sub>, ZnCl<sub>2</sub>, MgCl<sub>2</sub>, BF<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, HClO<sub>4</sub> combined with hydrogenation catalysts.

Hydrogenation catalysts: oxides or sulfides of the 6th group of the Periodic System, e.g., Mo oxide (2.5 parts) + H<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (70 parts) + kieselguhr (30 parts).

H<sub>2</sub>SO<sub>4</sub> + NiO + Fe.

NiO + ZnCl<sub>2</sub>.

NiO + AlCl<sub>3</sub>.

H<sub>2</sub>PO<sub>4</sub> on kieselguhr.

**Isomerization**

Al<sub>2</sub>O<sub>3</sub>.

Acids: HCl, H<sub>3</sub>PO<sub>4</sub>, HClO<sub>4</sub>.

Metallic Na, Cu.

Alcoholic potash.

Surface active substances: floridin, soda lime in Fe tube, silica gel, bauxite.

**c. Acetylene.****Hydrogenation (Continued)**

Pt on silica gel, ton, or pumice.  
Pd (H<sub>2</sub> dissolved in it) (activated wire, colloidal).

Pt on silica gel, ton, kieselguhr.

Ni-Pd (10 : 1) on charcoal, ton.

Ni, Co, Cu, Fe, Cr on kieselguhr.

Ni on active charcoal, ton, kieselguhr, activated by ThO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>.

Cu suboxide on charcoal.

Metallic Cu on silica gel.

Co alkali-Fe.

Cu(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> + cuprene formed.

Co or Fe entirely free from Ni (180°).

Ce or CeO<sub>2</sub> + active charcoal asbestos, kieselguhr.

Al powder.

**Chlorination**

Oxides (Fe, Si, Ti, Th, Zr, Al, Ni) on charcoal, silica gel, bauxite, coke pieces (2-3 cm.).

Halides (Bi, chiefly chlorides, Fe, Zn, Hg, Sb) on silica gel.

Melts of metal chlorides: AlCl<sub>3</sub>, FeCl<sub>3</sub>, NaCl (eutectic melts).

**Polymerization**

H<sub>2</sub>PO<sub>4</sub> (colloidal P).

AlCl<sub>3</sub>, (AlCl<sub>3</sub> · C<sub>2</sub>H<sub>5</sub> compounds formed).

Al<sub>2</sub>Cl<sub>6</sub> · Et<sub>2</sub>O · C<sub>2</sub>H<sub>2</sub>, or Al<sub>2</sub>Cl<sub>6</sub> · 2PhNMe<sub>2</sub> (both inactive).

Cu.

Cu<sub>2</sub>Fe(CN)<sub>6</sub> · 7H<sub>2</sub>O.

Mixtures:

CuCl<sub>2</sub> + NH<sub>4</sub>Cl.

Cu<sub>2</sub>Cl<sub>2</sub> + NH<sub>4</sub>Cl.

Cu on pumice.

Fe.

Mixtures:

Fe + Mg.

Fe + Ni (9 : 1).

Pt (150°).

**Polymerization (Continued)**

Cr sponge.

Ni.

Ni, Ag, or Mo on active charcoal.

Alkaline earths.

Chlorides.

Ca phosphate.

Surface active substances: porcelain filled with kieselguhr or charcoal, charcoal, bauxite, clay, glass.

Active birch and basswood, graphite contacts, japanesec acid earth.

**Isomerization**

Al<sub>2</sub>O<sub>3</sub>.

Alcoholic potash or soda.

Na alcoholate.

**Condensation with H<sub>2</sub>S**

Al<sub>2</sub>O<sub>3</sub>.

Hydrated Al<sub>2</sub>O<sub>3</sub>.

Al<sub>2</sub>O<sub>3</sub> activated by oxides, sulfides, or selenides of the 1st or 8th group of the Periodic System.

Zn or Cd (oxides or sulfides) mixed with activator Al<sub>2</sub>O<sub>3</sub> (chromates, tungstates, molybdates).

Oxides (Cu, Mn, V, Ti, Cr).

Hydroxides (Cu, Mn, V, Ti, Cr) on clay, kieselguhr, fuller's earth (may contain Fe compounds or hydrated Al silicate).

Salts of Hg, Ag, Sn, Cu + silicic acid.

**Condensation with NH<sub>3</sub>**

Oxides (Ti, Al, Zr, V, Si).

Hydrated oxides (Fe, Co, or V).

Metal (silicates, oxides, hydroxides, sulfides).

Cu, Hg, Zn, Cd, Co, Fe (formates containing acetates) on coke, diatomite, silica gel.

Zn (chloride) (anhydrous), sulfate on silica gel.

Fe rodanide on diatomite.

Table 3 (Continued).

**Condensation with  $NH_4$  (Cont'd).**  
Silicic acid + Al gel.  
Bauxite, permutite, active charcoal, mud and Fe ore.

**Condensation with  $H_2S$  or  $HCN$**   
 $Al_2O_3$  (hydrated).  
Metals (Ni) (oxides, sulfides).  
Alkalies or alkaline earths,  $NH_4$ , or heavy metals (sulfides or polysulfides).  
Cyanides (Ba) on charcoal.  
Adsorbents: bauxite, clay, fuller's earth.

**Condensation with Amines**  
Salts capable of giving ammoniates on silica gel and  $Al_2O_3$  acting as a dehydrating agent.  
 $ZnBr_2$  on pumice.

**Condensation with Aromatic Amines**  
Ammoniates on porous carriers.  
 $Al_2O_3$ .  
Halides, chiefly chlorides (Al, Cu, Hg).

#### Dehydration

$Al_2O_3$ .  
Surface-active substances: Japanese acid earth, bleaching earth, kieselguhr, activated birch wood.  
 $ZnCl_2$  on charcoal.

#### Oxidation

Oxides (Th, Mo, V, Sn, Cr, W, Co, Fe, Mn).  
Cu, Fe, Mn.  
Cu 100 times more active than Co. and Mn.  
Mixtures:  
Mo oxide + U oxide.  
90%  $V_2O_5$  + 10%  $UO_3$  on pumice.  
HgO + boric acid.  
Hg in conc.  $H_2SO_4$ .  
SeO<sub>2</sub> in conc.  $H_2SO_4$ .  
Surface active substances: silica gel, activated charcoal.

#### Hydrogenation

Ni (Raney's Ni).  
Ni (oxide, carbonate).  
Ni on kieselguhr.  
Ni on silica gel.  
Ni- $Al_2O_3$ .  
NiO- $Al_2O_3$ .  
Mixtures:  
Ni (25 g.) dissolved in  $HNO_3$  + Pd dissolved in  $HNO_3$  + silica gel (25 g.).

#### Hydrogenation

Ni.  
 $Ni_2O_3$ .  
Ni-Al.  
Pt, Pd (black and oxide).  
Acids (molybdic, vanadic, tungstic, phosphoric).  
Active charcoal, fuller's earth, kieselguhr, alumina.

#### Condensation with Aromatic Amines (Continued)

HgBr<sub>2</sub>.  
HgNO<sub>3</sub>.  
HgSO<sub>4</sub>.  
Hg<sub>2</sub>SO<sub>4</sub>.  
Hg(CN)<sub>2</sub> (not suitable).

**Condensation with (1)  $CH_4$ , (2)  $C_2H_4$ , and (3)  $CH_3COOH$**   
(1) Oxides (Si, Ti, Al, Ni, Co, Fe).  
Salts (Cu, Al, Hg).

(2)  $Al_2O_3$ .  
Ni on  $Al_2O_3$ .  
Active charcoal.

(3) Metal salts of oxygen containing strong acids on silica gel.  
HgSO<sub>4</sub> on Japanese acid clay.

**Condensation with (1) Alcohols and (2) Ethers**  
(1) Metal oxides on charcoal, kieselguhr.  
Metal salts of oxygen containing strong acids on silica gel.  
Alkali (oxides, hydroxides, cyanides).

#### d. Aromatics.

#### Dehydrogenation (Continued)

Pd, Pt.  
Pd, Pt (oxides, black).  
Pd in HCl (solution).  
10% Pd-asbestos.  
Al (chloride, oxide).  
Mo (oxide, sulfide).  
MoO<sub>3</sub> +  $Al_2O_3$ .  
Cu (oxide, sulfate).  
CuO- $Al_2O_3$ .  
Oxides, phosphides, nitrides, sulfides (Mo, W, Cr, V, Mn, Co, Ni, Fe, Zn, Rh, U, Sn).  
Charcoal impregnated with  $ZnCl_2$ , HCl, or  $H_3PO_4$ .

#### Dehydrogenation

Oxides (Zn, Mo, Ce, Al, W, U, Mg, Cr, Si).  
Pt, Pd black on charcoal.  
Mixtures:  
Zn- $Al_2O_3$ .  
Zn- $Al_2O_3$ .  
CdS, ZnS or  $Cr_2O_3$  mixed with  $Al_2O_3$ .  
ThO<sub>2</sub>-CoO + potash on pumice.  
Aliphatic oxy-acids mixed with Mn salts or other inorganic catalysts.  
Active charcoal impregnated with:  
(1)  $NH_4$  molybdate,  $Pb(NO_3)_2$  and  $H_3PO_4$  and treated with  $H_2S$  at 300°.  
(2)  $NH_4$  tungstate,  $Co(NO_3)_2$  and  $Sb_2O_3$  and treated with  $H_2S$  at 350°.

#### e. Terpenes.

#### Dehydrogenation

Metals splitting off  $H_2$ .  
Substances splitting off water:  
 $Al_2O_3$ , active charcoal, fuller's earth, kieselguhr.  
Ni + (0.14%)  $Na_2O$ .  
Ni + (0.5-1%)  $NaNO_3$ .  
Cu.  
Cu + alkaline earths.  
Charcoal containing Fe.  
Platinized charcoal.  
Metallic salts (the hydroxides of which are soluble in excess  $NH_3$ : Zn, Cu, Ag, Cd) such as nitrates (Cu, Zn, Cd, Ag).  
 $Al_2O_3$ .  
Al gel.  
Active charcoal.

#### Condensation with (1) Alcohols and (2) Ethers (Continued)

nides, zincate, alcoholate, phenolate, the latter three on active charcoal).  
Freshly precipitated HgSO<sub>4</sub>.

(2) Hydrolyzable metal halides ( $BiCl_3$ ).  
Halogenated ethers (chlormethyl ether).

**Condensation with Carbonic Acid**  
Silicates of phosphates of difficultly reducible metal oxides.  
Zn or Cd salts on charcoal, kieselguhr, silica gel.

**Condensation with Aromatic Hydrocarbons**  
Mixture of difficultly and readily reducible oxides on kieselguhr, charcoal, silica gel.  
Oxides (Si, Ti, Al).  
Cu<sub>2</sub>Cl<sub>2</sub>.  
Other salts of Al, Hg, Ni, Co, Fe.  
Zn or Cd salts of organic acids on active charcoal, pumice.

#### Dehydrogenation (Continued)

(3)  $NH_4$  vanadate,  $Co(NO_3)_2$  and  $H_3PO_4$  and treated with  $H_2$  and  $CS_2$  at 350° ( $UO_2$  may be present).

#### Alkylation

$AlCl_3$ .  
Halides (Be, B).  
Dioxyfluorboric acid,  $HBF_3(OH)_2$  and/or  $BF_3$  addition compounds may be used instead of  $BF_3$ .  
Anhydrous  $P_2O_5$ .  
Activated silicates, bleaching earth, clay, kaolin, tonsil.  
Kaolin activated with acids; heated for a few hours with  $H_2SO_4$  (25%) at 100-220°.  
Mixtures of oxides:  
50%  $Al_2O_3$  + 50%  $Fe_2O_3$ .  
30%  $Al_2O_3$  + 70%  $Fe_2O_3$ .  
ThO<sub>2</sub>.

#### Isomerization

Oxides ( $Al_2O_3$ ,  $Ni_2O_3$ ).  
Chlorides ( $AlCl_3$ , HCl).  
30% Pt on charcoal.  
Pd.  
Activated silicates, activated hydrosilicates (treated with acids).  
Kieselguhr, natural and activated earths (infusorial earth, bleaching earth, Japanese acid earth).  
Acid-free ton or kaolin.

#### Isomerization

Active charcoal.  
Earths (Japanese acid earth, florida, floridin, bleaching, fuller's).  
Acid ton.  
Silica gel.  
50% Activated charcoal.  
Acids:  
5-15% : 70%  $H_3PO_4$ .  
65-75%  $HCOOH$ .  
90-100%  $CH_3COOH$ .  
HCl, oxalic and tungstic acids.  
Alkalies.  
Platinized charcoal.  
Pd black.

Table 4. Groups of Catalysts Typical of Reactions of Aldehydes, Ketones, Acids, Alcohols, Nitro-compounds, Ethers and Esters.

## a. Aldehydes.

<i>Synthesis</i>	<i>Reduction (Continued)</i>	<i>Hydrogenation (Continued)</i>
(1) Formaldehyde: Ag, Cu, Fe, or their oxides. Mixture Ag-Cu, Rh + Ag + Cu. Mixture of oxides: Fe <sub>2</sub> O <sub>3</sub> + Cr <sub>2</sub> O <sub>3</sub> . Fe <sub>2</sub> O <sub>3</sub> + MnO <sub>2</sub> . CuO + Cr <sub>2</sub> O <sub>3</sub> . Oxides on carriers: pumice, asbestos.	Pt (black, oxide). Metallic salts (the hydroxides of which are soluble in an excess of NH <sub>3</sub> ) on carriers (kieselguhr, alumina, or silica gel, active charcoal, fuller's earth).	Ni (prepared from NiSO <sub>4</sub> and soda). Ni—kieselguhr. Ni(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O—kieselguhr. Cu, Cu on water glass. Pt oxide.
(2) Acetaldehyde: Oxides (Cu, Ag). Hg compounds. Chlorides (Ca, Mg). MgSO <sub>4</sub> (free from water of crystallization). Phosphates, borates and silicates.	<i>Oxidation</i> (1) Acetaldehyde: Ozone. Acetates (Mn, Ni, Na, Cu, Cr, Co). Mn. Mixtures: Na acetate + Fe <sub>2</sub> O <sub>3</sub> . Na acetate + bone charcoal. Cr acetate + Co acetate. Co acetate (0.002%) + Mn acetate (0.2%). Mn acetate + Mn nitrate. Oxides (Mn, V, Ce, Mo). Mixture of oxides (Fe, Mn, Cu, Ni, Zn) with halides of these metals. Compounds of Fe + alkali salts or organic acids. Pt (black). Pt (Al, V) on asbestos or pumice (inactive at low temperature). Ca (phosphate). Kieselguhr, kaolin, bone charcoal, ash, silica aerogel.	(2) Benzaldehyde: Fe. <i>Condensation</i> (1) Acetaldehyde with H <sub>2</sub> S: Al <sub>2</sub> O <sub>3</sub> . TiO <sub>2</sub> on charcoal. (2) Propionaldehyde with NH <sub>3</sub> : Al (oxide, hydroxide). Base-exchanging compounds. Piperidine. (3) Formaldehyde with urea: ZnCl <sub>2</sub> . Oxides on silica gel. Hexamethylenetetramine. (4) Formaldehyde condensed to sugars: Mg, Zn. CaO, NaOH. Glass, tropical sunshine. Monose.
(3) Benzaldehyde: Chlorides (Al, Cu) (water free). Mixture AlCl <sub>3</sub> + CuCl <sub>2</sub> . Hydroxides (Al, Sb). Oxides (Fe, Zn).	(2) Butyraldehyde: Mn salts. Mn butyrate. Mn butyrate on carriers: chamotte, pumice, alumina, ton pieces.	(5) Formaldehyde with isobutyraldehyde: Alkaline substances.
<i>Decomposition</i> (1) Formaldehyde: Pd, Rh, Ru, Os, Rh black. Al alcoholate.	(3) Benzaldehyde: Oxides (Ni, Co, Cu). Ozone (O <sub>3</sub> more active in pure O <sub>2</sub> than in an O <sub>2</sub> -N <sub>2</sub> mixture).	(6) Benzaldehyde with (a) phthalic anhydride; (b) orthoethyl formate; (c) chloral hydrate: ZnCl <sub>2</sub> .
(2) Acetaldehyde: Hg (oxide, sulfate, phosphate (the latter in H <sub>3</sub> PO <sub>4</sub> )). I <sub>2</sub> , Br <sub>2</sub> . HCl, H <sub>2</sub> S, NO. Strong acids on carriers. Small amounts of ether. Ni (Cu, Fe, Co). Zn, ZnCl <sub>2</sub> .	<i>Hydrogenation</i> (1) Crotonic aldehyde: Ni (Raney's Ni; suspended in a sulfur-free mineral oil, chromate, nitrate).	(7) Claisen's self-condensation of aldehydes: Alcohol-free Al alkoxides.
(3) Propionic aldehyde: 1. Pt surface.		(8) Cinnamic aldehyde with benzyl alcohol: Al. Benzyl oxide. Alkali benzyolate.
<i>Dehydration</i> Al <sub>2</sub> O <sub>3</sub> . Terpene aldehydes: Active charcoal.		
<i>Reduction</i> (1) Aromatic aldehydes: Pd chloride.		

## b. Ketones.

<i>Synthesis</i>	<i>Reduction</i>	<i>Hydrogenation (Continued)</i>
Metal oxides (Al, Th, Mn, Ca, Ba, Sr, Cr, Ti, Mg) (difficultly reducible). Metals Fe, Cu, Co, Ni, or their oxides. Ag. Mixtures: 15% Cu formate + 1.8% Mo oxide. Cd vanadate + FeO. Vanadates (Zn, Cd). Chromites (Mn, Zn).	Alloys: Cu-Cr, Zn-Cr. Cu (oxide, chromite, nitrate). Cu (Ni) on kieselguhr or silica gel. Mixtures: Cu nitrate + NH <sub>3</sub> chromate neutralized with NH <sub>4</sub> OH. Cr on kieselguhr. Zn dust. Oxides (Zn, Mg, Al, Si, Ti, Se) mixed with K <sub>2</sub> O <sub>3</sub> . AlCl <sub>3</sub> (anhydrous). Pt, Pd on charcoal. Pt-PtO <sub>2</sub> . Pd on bone charcoal. Charcoal impregnated with 10% Pt and alcoholic solution of PdCl <sub>2</sub> . Base exchangers, permutogenetic material.	Pd. Pt black. Pt-PtO <sub>3</sub> . Zr, Ca. Oxides (Al, Th, Mo). Amalgams (Al, Mg). Alloys: Zn-Cu (prepared from Cu-ZnO-Cr <sub>2</sub> O <sub>3</sub> ). Alkali. Yeast. p-Xyline.
<i>Decomposition</i> Chlorides (Zn). Fe tube. Alkali (alkali sulfates + alkali bisulfates).	<i>Hydrogenation</i> Ni (Raney's Ni). NiO (more effective than reduced Ni). Ni on kieselguhr.	<i>Chlorination</i> AlCl <sub>3</sub> . <i>Condensation with Alcohol</i> Al <sub>2</sub> O <sub>3</sub> . Al <sub>2</sub> O <sub>3</sub> impregnated with 15% Cu formate + 1.8% MoO <sub>3</sub> . OH and ions of bases. Acids (HCl, H <sub>2</sub> SO <sub>4</sub> ). Solid KOH. Na in xylene. Na in benzene.
<i>Dehydration</i> Oxides (Al, Ni). Mixture: NiO + Al <sub>2</sub> O <sub>3</sub> (terpene ketones).		



Table 4 (Continued).

## c. Acids.

- Synthesis**
- (1) Formic acid:  
Chlorides (Ca, Cu).  
 $\text{CaI}_2$ , NaBr.  
Oxides (Cr, Cu, Li, Ni).
- (2) Acetic acid:  
(a) from acetaldehyde;  
Acetates (Mn, Cu).  
Co, Cr, Cu.  
Mn + Fe.  
(b) from CO and methanol;  
Mixtures:  
 $\text{W}_2\text{O}_5$  + nitrates (Be, Bi, Zn, Cu, Al, Ce, Th).  
 $\text{WO}_3$  +  $\text{Al}_2\text{O}_3$  +  $\text{Bi}_2\text{O}_3$  + Zn.  
2% Cu phosphate + 87%  $\text{H}_3\text{PO}_4$ .  
 $\text{CuO}$  +  $\text{Cr}_2\text{O}_3$ .  
Hydrogen halide on charcoal.  
(c)  $\text{Hg}(\text{NO}_3)_2$  +  $\text{CeO}_2$ .  
 $\text{HgO}$ .  
 $\text{BF}_3$ .
- (3) Propionic acid from CO and olefinic hydrocarbons:  
Volatile halides.  
 $\text{NH}_4\text{Cl}$  on activated charcoal.  
Chlorides (Ca, Zn) on activated charcoal.  
 $\text{Cl}_2$  on activated charcoal.  
 $\text{HCl}$  on activated charcoal.  
B phosphate.  
Oxides (Mo, P, As, W, U, Cr, V, Ti, Zr, B).  
Mixtures of oxides:  
 $\text{MoO}_3$  +  $\text{Cr}_2\text{O}_3$ .  
 $\text{H}_2\text{SiO}_4$  +  $\text{H}_2\text{MoO}_4$  + Cr vanadate.
- Decomposition**
- (1) Formic acid:  
O<sub>2</sub> and Ru.  
Rh, Ir black.  
Cu.  
Cu-Au (mixed crystals).  
Cu<sub>2</sub>Au.  
Cu-Pd } alloys.  
Cu-Au.  
Acids:  $\text{H}_2\text{SO}_4$  mixed with  $\text{H}_2\text{SeO}_4$ .
- (2) Acetic acid:  
Oxides (Al, Th, U, Zn, Cr, Mn).  
Oxides of alkali earths (Ca, Ba).  
Carbonates and acetates (Ca, Ba).  
Mixtures:  
 $\text{Ca}(\text{OH})_2$  + MgO.  
Phosphates (Th, Mn, Mg, Ca, K, Ba).  
Alkali phosphates (melts).  
Cu, Al, V, 2A-steel containing carbon.  
Ceramic masses.  
Strong acids ( $\text{H}_2\text{SO}_4$ ) and bases.
- (3) Fatty acids:  
Os, Ru, Rh, Ti, Pt, Ir, Rh, Pd, Th.  
Oxides (Zn, Ti).  
Cu-Au (mixed crystals).
- Decomposition (Continued)**
- (4) Oleic acid.  
Oxides (U, Al).  
Zr, silica.
- (5) Stearic acid:  
Sulfurized naphthenes.
- (6) Propionic acid:  
Carbonates (Zn, Ca).
- (7) Oxalic acid:  
 $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ .
- (8) Phthalic acid:  
Carbonates (Na, Ca).  
Sulfates (Cu).  
Mixtures of oxides:  
 $\text{CdO}$  +  $\text{Al}_2\text{O}_3$  +  $\text{H}_2\text{O}$  vapor.
- Dehydration**
- (1) Formic acid:  
 $\text{H}_2\text{SO}_4$  (at 15%).  
Oxides (mixtures) ( $\text{ThO}_2$ - $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ - $\text{SiO}_2$ ,  $\text{TiO}_2$ - $\text{SiO}_2$  + Al phosphate).
- (2) Acetic acid:  
Oxides (Al, Fe, Mn, Zn, Th, U).  
 $\text{ThO}_2$  on pumice.  
Phosphates (alkaline earths).  
Metaphosphates (Na) alone or together with Li carbonate (melt).  
Pt on silicic acid skeleton or charcoal.  
Au tube filled with activated charcoal.  
 $\text{H}_3\text{PO}_4$  on pumice, (kieselguhr, Carborundum).  
Au tube filled with activated charcoal.  
Quartz.
- Reduction**
- Ni.  
Ni (oxide, carbonate).  
Mixtures:  
 $\text{NiO}$  +  $\text{Al}_2\text{O}_3$ .  
Ni carbonate (Cr, V compounds used as activators) on kieselguhr.  
 $\text{NiO}$  on silica gel.  
Cu, 15% Cu + 85% kieselguhr.  
Cu (carbonate).  
Cu + Th (Cr).  
Oxides (Mn, Cd, Co, Zn, Sn, Mg).  
Pd black.
- Oxidation**
- (1) Formic acid:  
Hydroxides and oxyhydrates without active hydrogen ( $\text{Fe}^{++}$ ).
- (2) Acetic acid:  
Fe (orthohydroxide).
- (3) Oxalic acid:  
Fe.  
Mn salts.  
Charcoal (blood, sugar).
- Oxidation (Continued)**
- (4) Butyric acid:  
Mixtures:  
K phosphate + Co.  
 $\text{MnO}_2$  +  $\text{H}_3\text{PO}_4$  ( $\text{H}_2\text{SO}_4$ ).
- (5) Maleic acid:  
Sugar charcoal.
- (6) Amino acids.  
O<sub>2</sub>.
- Hydrogenation**
- (1) Fatty acids:  
 $\text{Ni}$  (finely dispersed, sponge).  
Ni (20%) on carriers (kieselguhr, silica gel, alumina, talcum, charcoal, ton, bone charcoal,  $\text{Ce}_2\text{O}_3$ ).  
Ni (oxides, borate, acetate, formate).  
Ni soap.  
Acetates, lactates (Cu, Fe, Co).  
Chromites (Zn, Cu).  
Cu (containing 20-60% Cd) on kieselguhr.  
Electric glow discharge.
- (2) Maleic acid:  
Rh on carriers (ceramics, blood charcoal).  
CuO, reduced Cu.  
Pt electroplated on polished Ni and Pt.
- (3) Phthalic acid:  
Na-Hg.
- (4) Various acids:  
Pd on blood charcoal (9 times more active than on kieselguhr).  
Fermented yeast.
- Chlorination**
- Chlorides (Al).  
Mixtures.  
 $\text{PI-PCl}_5$ .  
Mixtures of P, I, S, powdered Fe in acid.
- Condensation**
- (1) Acetic acid + phthalic anhydride:  
Na, K (acetates).
- (2) Maleic acid + cinnamic aldehyde:  
Amines.  
Amino acids.
- (3) Chlorbenzoic acid + aniline.  
Cu.
- (4) Oxystearic acid + glycol (fumaric, phthalic, adipic, monochloroacetic acids).  
Secondary amines more active than primary amines (weak bases, such as urea, inactive).
- Isomerization**
- Atomic iodine (in benzene).  
H ions.  
Nitrous acid.

## d. Alcohols.

- Synthesis**
- (1) Ethyl alcohol:  
Oxides (Fe, Co, Mn, Cu, Zn).  
Mixtures:  
CuO : MnO : CoS<sub>2</sub>  
(10 : 10 : 1).  
ZnO : CoO (3 : 1).  
CoO : CuO : MnO (0.05 mol : 1.0 mol : 1.0 mol).
- Synthesis (Continued)**
- MnO + 2H<sub>2</sub>PO<sub>4</sub>.  
FeO + 2H<sub>2</sub>PO<sub>4</sub>.  
Boric anhydride + H<sub>2</sub>PO<sub>4</sub>  
(1.0 mol : 2.2 mols).  
Halides:  
Chlorides (HCl, CH<sub>3</sub>Cl, CCl<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>Cl) on carriers.  
HI, HBr.
- Synthesis (Continued)**
- Acids ( $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ ).  
 $\text{H}_3\text{PO}_4$  + sulfates (Ag, Li).  
Cd metaphosphate.
- (2) Higher alcohols:  
Metal oxides (Zn, Mn, U, Al, Cr, Mo, Pb, Cu, Ni).

Table 4 (Continued).

Synthesis (Continued)	Dehydration (Continued)	Oxidation (Continued)
<p>Mixtures:  <math>\text{ZnO} + \text{Cr}_2\text{O}_3</math>.  <math>\text{ZnO} + \text{Mn}_2\text{O}_3 + \text{Cu}</math>.  <math>\text{MgO} + \text{Al}_2\text{O}_3 + \text{CuO}</math>            (89 : 8 : 3).            Basic Zn chromate + Co            chromate (10%).  <math>\text{I}_2</math> (perchromate, perborate).            Cu (chromate, formate, acetate).  <i>Volatile halides</i> (<math>\text{HCl}</math>, <math>\text{HI}</math>, <math>\text{HBr}</math>,            or <math>\text{CH}_3\text{Cl}</math>, <math>\text{C}_2\text{H}_5\text{Cl}</math>, <math>\text{CCl}_4</math>) on            carriers (pumice, silica gel,            coke).            Strong acids of moderate con-            centration (10%) (<math>\text{H}_2\text{SO}_4</math>,  <math>\text{H}_3\text{PO}_4</math>, <math>\text{HCl}</math>), acetic acid.</p>	<p>(4) Amyl and isoamyl alcohol:  <math>\text{Al}_2\text{O}_3</math> + various additions.  <math>\text{Al}_2\text{O}_3</math> + heavy metals of the 1st,            6th, 7th, and 8th groups.  <math>\text{Al}</math> silicate.            Mixtures:  <math>\text{Na}_2\text{HPO}_4</math> + red P.  <math>\text{NaH}_2\text{PO}_4</math> + <math>\text{Al}(\text{OH})_3</math>.            (5) Glycols:  <math>\text{Al}_2\text{O}_3</math> (<math>\text{NH}_3</math> aluminate calcined).  <math>\text{Al}_2(\text{SO}_4)_3</math>.  <math>\text{H}_3\text{PO}_4</math> or acid salts (<math>\text{NaH}_2\text{PO}_4</math>,  <math>\text{MgH}_2(\text{PO}_4)_2</math>).            Monophosphate (100 parts)            chemically active, on 25%            kieselguhr or bleaching earth            (graphite or coke).            Kaolin, bauxite.            Mixtures of metal oxides (5th-            7th groups) on kieselguhr or  <math>\text{Al}_2\text{O}_3</math>.            (6) Carbinols:  <math>\text{Al}_2\text{O}_3</math>.  <math>\text{Al}_2\text{O}_3</math> (from Na aluminate).  <math>\text{Al}_2\text{O}_3</math> on pumice.  <math>\text{H}_3\text{PO}_4</math> on silica gel.            Platinized charcoal.            Mixture:            40% infusorial earth +            30% ton + 30% cork flour            (mixed with water, dried            by heating to 900–1000°).</p>	<p>Cu on charcoal (2.1 : 1.5) (T,            below 100°).            Cu on pumice, asbestos.            CuO.            CuO + small amount <math>\text{NH}_3</math> on            active charcoal.            Cu tube with Pt.            Pt (black, oxide).  <math>\text{Na}_2\text{PtCl}_6</math> on asbestos.            Ru and its compounds.  <math>\text{Fe}_2\text{O}_3</math> (<math>\rho\text{H} = 0.7</math>).            Ferric ions.  <math>\text{V}_2\text{O}_5</math> on silicic acid gel or natu-            ral bleaching earth.  <math>\text{V}_2\text{O}_5</math>.  <math>\text{NaNO}_3</math> and <math>\text{KNO}_3</math> (melts).            Melted boric acid on silica gel            or kieselguhr.            Bone charcoal treated with <math>\text{I}_2</math>.            Benzoquinone, xylene.</p>
Decomposition		
<p>(1) Ethyl alcohol:  <i>Oxides</i> (Zn, Al, Si, Mg, W, U,            Ti, Se, Th, Ga).  <math>\text{KOH}</math>, <math>\text{K}_2\text{SO}_4</math>.            Heated <math>\text{Al}_2\text{O}_3</math> or clay, glowed            kaolin.            0.1–0.2% <math>\text{ThO}_2</math> containing <math>\text{CuO}</math>.  <math>\text{NiCrO}_4</math>.            Ni on pumice.  <math>\text{KCH}_3\text{NH}_2 &gt; \text{KC}_2\text{H}_5\text{NH}_2</math>  <math>&gt; \text{KCH}_3\text{NH}</math>.</p>	<p>(7) Hydroaromatic alcohols:  <math>\text{Al}_2\text{O}_3</math>.            Earths (japanese acid, bleach-            ing).            Silica gel (not active).            Activated birch.  <math>\text{ZnCl}_2</math> on charcoal.</p>	<p>(2) Higher alcohols:            Cu.            Cu (finely dispersed) on ton or            kaolin.            Cu plated on iron filings.            CuO (from melted CuO re-            duced at 200° with <math>\text{H}_2</math>).            Steel wool.            Zn phosphide.</p>
Dehydration		Reduction
<p>(1) Ethyl alcohol:  <i>Oxides</i> (Al, Th, W, Zn, Ag, Cu).  <math>\text{Al}_2\text{O}_3</math> (Kahlbaum).  <math>\text{Al}_2\text{O}_3</math> (precipitated alumina            heated below red heat).            Glassy alumina.            Alumina with 5.5% by weight            of <math>\text{H}_2\text{O}</math> pure <math>\text{Al}_2\text{O}_3</math> (the xero-            gel 18 times more active than            the aerogel).  <math>\text{Al}_2\text{O}_3</math> impregnated with <math>\text{H}_3\text{PO}_4</math>.            Mixtures of oxides:  <math>\text{Al}_2\text{O}_3 + \text{CuO}</math>.  <math>\text{Al}_2\text{O}_3 + \text{NiO}</math>.  <math>\text{CuO} + \text{Ag}_2\text{O}</math>.  <math>\text{Al}_2\text{O}_3</math> + sulfates, such as  <math>\text{CuSO}_4</math>. (+ <math>\text{Na}_2\text{CO}_3</math> added            dropwise).  <math>\text{Al}_2\text{O}_3 + \text{Cr}</math> anhydride.  <math>\text{Al}_2\text{O}_3</math> + birch wood.            Na aluminate.            Selenides.            Phosphides.            Glassy clay with activators:            Ni, Cu, Ag, <math>\text{CuO}</math>, <math>\text{Cr}_2\text{O}_3</math>,  <math>\text{MnO}</math>, <math>\text{ZnS}</math>, <math>\text{CoS}</math>.  <math>\text{K}_2\text{CO}_3</math> (anhydrous).            Mg phosphate on fine grain            coke.            Metallic Ca.            Na aluminate.            Active earths (bleaching,            japanese acid).</p>	<p>(8) Cyclic and bicyclic terpene            alcohols:  <math>\text{Al}_2\text{O}_3</math>.  <math>\text{Al}_2\text{O}_3 + \text{CuO}</math> (small amount).            Earths (japanese acid, bleach-            ing, florida).            Kieselguhr, active charcoal, ka-            olin.            Cu carbonate.            (9) Joint dehydration of alcohol            and ammonia or anilin:  <i>Oxides</i> (Al, W, Fe, Ti, Zn, Sn,            Cu, Zr, Ce, Ni).  <math>\text{WO}_3</math> on kaolin.  <math>\text{CeO}_2</math> on pumice.  <math>\text{ThO}_2</math> on silica gel.  <math>\text{NiO}</math> on silica gel.            Mixtures:            90% <math>\text{Al}_2\text{O}_3 + 10\%</math> <math>\text{Fe}_2\text{O}_3</math>.            90% <math>\text{Al}_2\text{O}_3 + 10\%</math> <math>\text{SnO}_2</math>.            90% <math>\text{Al}_2\text{O}_3 + 10\%</math> <math>\text{ZnO}</math>.            80% <math>\text{Al}_2\text{O}_3 + 20\%</math> <math>\text{Cr}_2\text{O}_3</math>.            Pure alumina + oxides of met-            als used in hydrogenation.  <math>\text{K}_2\text{CO}_3</math> (anhydrous).            Hydrosilicates.            Silicic acid, bauxite.</p>	<p>Higher alcohols:            Ni.            Ni (from <math>\text{NiBr}_2</math>).            Ni on kieselguhr.            Ni + NiO (50%) on kieselguhr            (Cu, Co, or Fe may be added).            Ni + <math>\text{Al}_2\text{O}_3</math>.            NiO + <math>\text{Al}_2\text{O}_3</math>.            Ni formate.            Cu. Cu obtained from Cu ox-            idate 5 times more active than            that obtained by reduction            from <math>\text{CuO}</math>.            Reduced Cu on silica gel or kie-            selguhr.            Cu + <math>\text{MgCO}_3</math>.            Mg (in ether).            Zn (dust).            Fe (from <math>\text{FeCl}_3</math>).            Co on kieselguhr.            Pt, Pt oxide.            Pt or Pd on charcoal or kiesel-            guhr.</p>
<p>(2) Propyl and isopropyl alcohol:  <i>Oxides</i>.  <math>\text{Al}_2\text{O}_3</math> (highly heated).            Ca phosphate.</p>		Dehydrogenation
<p>(3) Butyl and isobutyl alcohol:  <i>Phosphates</i> (<math>\text{Na}_2\text{PO}_3</math>, <math>\text{Na}_2\text{HPO}_4</math>,  <math>\text{MgH}_2(\text{PO}_4)_2</math>).            90% <math>\text{H}_3\text{PO}_4</math> on alumina or pum-            ice stone.  <math>\text{Na}_2\text{PO}_3</math> on bauxite.  <math>\text{ZnCl}_2</math>.</p>	<p>(1) Ethyl alcohol:            Ag (wire, net [red heat]).            Ag on brown coal, pitch.            Ag + 0.14% or 0.27% <math>\text{Sm}_2\text{O}_3</math>.            Ag + Cu (4 : 1).            Silicic acid gel containing            Ag + CuO.  <i>Oxides on charcoal</i>:  <math>\text{ZrO}_2</math> (<math>\text{ThO}_2</math>)  <math>\text{Cr}_2\text{O}_3</math> (<math>\text{ThO}_2</math>)  <math>\text{ZrO}_3</math> (<math>\text{ThO}_2</math>) + Cu } T. 63°.</p>	<p>(1) Ethyl alcohol:            Cu (finely dispersed).            Cu (made passive against side            reaction with CO by addition            of Ag).            Cu + Ag (equal parts) on silica            gel.            Cu-Zr (0.9%).            Cu finely dispersed or Ag, Co,            Zn, Pd, or Pt together with            a partially hydrolyzable salt            of an amorphous base or Mg            with an organic acid.            Cu (pure) activated with <math>\text{CeO}_2</math>,  <math>\text{ZrO}_2</math>, <math>\text{Al}_2\text{O}_3</math>.            Cu + <math>\text{CeO}_2</math> (0.2%).            Cu + <math>\text{ZrO}_2</math> (0.9%).            Cu tube filled with brass.  <math>\text{Al}_2\text{O}_3</math> (pure).            Mixtures with oxides:            (<math>\text{Fe}_2\text{O}_3</math>, <math>\text{NiO}</math>, <math>\text{Cr}_2\text{O}_3</math>, <math>\text{ZnO}</math>,  <math>\text{SnO}</math>).  <math>\text{Al}_2\text{O}_3</math> (90%) + <math>\text{Fe}_2\text{O}_3</math> (10%)            (most favorable).            Waste products from Al salts            (from clays by action of            acids).            Ru and its compounds.</p>

Table 4 (Continued).

<p><i>Dehydrogenation (Continued)</i> Alkalies, alkaline earths. Heavy metals melted with 10% <math>H_2PO_4</math> and boric acid. Oxides (V, U, Mo).</p>	<p><i>Dehydrogenation (Continued)</i> Re (addition of <math>ReS_2</math>; increase in phenol formation instead of cyclohexanone).</p>	<p><i>Condensation (Continued)</i> <math>Al_2O_3</math> on silica gel. Mixtures: ZnO : <math>Al_2O_3</math> : silica gel (20 : 10 : 72).</p>
<p>(2) Propyl and isopropyl alcohol: Zn. ZnO (as a paste coated on filings or small pieces of Cu, Al, brass, steel, carborundum). ZnS. Zn<math>P_2</math>. Zn-Cu. Cu. Cu (optimum dehydrogenating temperature, 300°). Cu (Fe, brass, Ag, Cr) finely dispersed on charcoal pieces. Cr-Ni. Cr-Mo. Steel tubes. Re. Re (layer of 2 g. pure metal; dehydrogenating temperature, 400°).</p>	<p><i>Dehydrogenation and Dehydration</i> Metal oxides (Be, Mg, Zn, Al, Si, Ti, Ge, Zr, Sn, Ce, Th, V, Bi, Cr, Mo, W, U, Mn, Fe) + basic substances (for dehydrogenation) (salts of alkalies or alkaline earths). <math>Al_2O_3</math> for dehydration accelerates the H—OH recombination. KOH, <math>K_2CO_3</math>, Zn-Cr<math>2O_3</math> (for dehydrogenation; insures H—H recombination). Ni + <math>Al_2O_3</math> (from chlorides, sulfates, or nitrates). ZnO and BeO. Fe<math>2O_3</math>, Cr<math>2O_3</math>.</p>	<p>(3) with olefins: <math>Al_2O_3</math>. Mixtures: <math>Al(OH)_3</math> + yellow tungstic acid. <math>H_2PO_4</math> + silicic acid. 10% free <math>H_2PO_4</math> + Ce salt of phosphorous-tungstic acid. Phosphorous-molybdic acid. Metaphosphates (Cr, Ce). Trimethyl or amyl amine.</p>
<p>(3) Butyl alcohol: Cu-U. ZnO (2 mm. grain). Re (from NaReO<math>_4</math> by the hydrazine method).</p>	<p><i>Chlorination</i> <math>Al_2O_3</math>. <math>H_2PO_4</math> on active charcoal. Silica gel.</p>	<p>(4) with acetylene: Metals, oxides on charcoal. Metallic salts of strong acids containing oxygen on silica gel. Alkalies (oxides, hydroxides, or cyanides). Alkalies (zincate, phenolate, alcoholate) on active charcoal. H<math>2SO_4</math> (freshly precipitated).</p>
<p>(4) Cyclic alcohols: Cu (Ni) on Al gel.</p>	<p><i>Condensation</i> (1) with <math>H_2S</math>: Oxides ThO<math>_2</math> (better than <math>Al_2O_3</math>). Bauxite, active charcoal, bleaching earth. (2) with nitro compounds: Oxides (Th, Zn, Al) on carriers (silica gel, asbestos). ThO<math>_2</math> on asbestos.</p>	<p>(5) with ketones: <math>Al_2O_3</math>. 15% Cu formate + 1.8% MoO<math>_3</math> impregnated on <math>Al_2O_3</math>. (6) with benzene: AlCl<math>_3</math>. Active bleaching earth.</p>
<i>Synthesis</i>		
<p>(1) Amino compounds: Al (oxide, hydroxide, phosphate, silicate). <math>Al_2O_3</math> + Fe<math>2O_3</math>. <math>Al_2O_3</math> · SiO<math>_2</math>. <math>Al_2O_3</math> on silica gel. <math>Al_2O_3</math> on chromium gel. Oxides (Th, B, W, Ti) on silica, chromium, alumina gel. P-containing compounds: P<math>_2O_4</math>, phosphates, <math>H_2PO_4</math>.</p>	<p>e. Nitro-compounds. <i>Reduction (Continued)</i> Co (hydroxide, molybdate) alone or on asbestos. Co-Mn. Co-Cr (not very active). <math>Al_2O_3</math>. <math>Al_2O_3</math> on kieselguhr. Ni nitrate (70°) on silica gel + dilute Na<math>2CO_3</math>. Active silica or Al gel. Bleaching earth. SiO<math>_2</math>.</p>	<p><i>Oxidation (Continued)</i> Cu or Os anhydride. Cu (sulfide or sulfate).</p>
<p>(2) Nitriles: <math>Al_2O_3</math> (TiO<math>_2</math>). <math>Al(OH)_3</math> (granulated). Hydrogen halides (also BaCl<math>_2</math>). Japanese acid earth, silicic acid gel.</p>	<p>(2) Aromatic nitro-compounds: Ni (reduced), 0.52 g. Ni for 1 g. of compound reduced). Mixtures: Ni nitrate + oxides (difficultly reducible Al, Zn, or Ag, Cu, Fe) on carriers (kieselguhr, pumice, silicic anhydride). Ni dispersed in methyl oleate or palmitate.</p>	<p><i>Hydrogenation</i> (1) Nitriles: Ni. Ni on silica gel. Ni in the presence of NiSO<math>_4</math>. Cu (oxide, hydroxide, carbonate) on bleaching earth, silica gel or charcoal. Cu-silicic acid on pumice. Cu-silica gel. Pd (finely dispersed). Pd on charcoal. Ni (Raney's). Ni (oxide, formate). Nion kieselguhr + small amount of alkaline substances. Raney's Ni + PbO<math>_2</math>. Ni + (methyl oleate, palmitate, or high boiling paraffins). Pd on bone charcoal. Platinized Pt (activated by dilution with HCl).</p>
<i>Decomposition</i>		
<p>(1) N<math>_2</math>O: CuO. Mixtures: CuO-<math>Al_2O_3</math>. CuO-TiO<math>_2</math>. Fe<math>2O_3</math> + <math>Al_2O_3</math> (bauxite). Pt (Ag). NiO.</p>	<p>Cu. Cu (oxide, carbonate, chromate). Pt (oxide, black) (their mixture). Pd on kieselguhr or charcoal. Suspension of Pd black (2 g.) in acetic acid (100 cc.) + 2 cc. conc. <math>H_2SO_4</math> with <math>H_2</math> under 3 atm. pressure. Zn (dust, in acetic acid). ZnCl<math>_2</math>. V<math>2O_5</math>.</p>	<p>(2) Nitrobenzene: Ni. <math>Al_2Ni</math> } alloys with either 27% <math>Al_3Ni</math> } Ni or 73% Ni. <math>AlNi</math> } Double chromite from NH<math>_3</math> and Ni. Pd. Ag or Au (or mixture of both). Cu. Cu + 10% CaO. Ag, (Au), Fe, Zn with Cr<math>2O_3</math> or MnO<math>_2</math>. Metallic salts precipitated by SiO<math>_2</math>. Carbon.</p>
<p>(2) NH<math>_4</math>NO<math>_3</math>: Acids (acetic, hydrochloric, formic, salicylic, anions of these acids). Pt } colloidal. Au }</p>	<p>(3) Azo compounds: Fe, Cu (Hg). SnCl<math>_2</math>.</p>	
<p>(3) Na<math>N_3</math>. Sulfohydril compounds.</p>	<p><i>Reduction</i> (1) Nitrobenzene: CuO (with butyl alcohol). Cu(OH) on silica gel.</p>	
<i>Reduction</i>		
<p>(1) Nitrobenzene: CuO (with butyl alcohol). Cu(OH) on silica gel.</p>	<p><i>Oxidation</i> Amines: V<math>2O_5</math>.</p>	

Table 4 (Continued).

<p><i>Hydrogenation</i> (Continued)</p> <p>(3) Aromatic amines:  <i>Ni</i> (Raney's).  <i>Ni</i> on silica gel.  Soluble <i>Ni</i> on kieselguhr (treated with basic carbonate).  <i>Ni</i> carbonate (precipitated and reduced).  <i>Pt</i> (oxide, black).  Alkalies.  Alkaline earths.  <math>\text{Na}_2\text{CO}_3</math>.</p> <p>(4) Aromatic nitro compounds:  <i>Pd</i> asbestos.  <math>\text{CuSO}_4</math>.  Mixture:  25 g. <i>Ni</i> dissolved in <math>\text{HNO}_3</math> + <i>Pd</i> in <math>\text{HNO}_3</math> + 25 g. silicic acid gel.</p> <p><i>Dehydrogenation</i></p> <p>Amino acids:</p>	<p><i>Dehydrogenation</i> (Continued)</p> <p>Alloxan.  Quinone.  Isatine and its derivatives:  <i>n</i>-methyl isatine.  isatine-5-sulfo acid.  isatine-chlorine.  isatine-bromine.</p> <p><i>Pt</i>.  Platinized charcoal.  Mixtures.  <i>Zn</i> arsenate + <i>Cd</i> arsenate.  <i>Ni-Al}_2\text{O}_3.</i></p> <p><i>Alkylation</i></p> <p>(1) Aromatic amines:  Activated silicates:  bleached earth, clay, tonsil, kaolin with acids (heated with <math>\text{H}_2\text{SO}_4</math> for several hours at 100–220° for activation).</p>	<p><i>Alkylation</i> (Continued)</p> <p><math>\text{ThO}_2</math>.  Mixtures of oxides:  50% <math>\text{Al}_2\text{O}_3</math> + 50% <math>\text{Fe}_2\text{O}_3</math>.  30% <math>\text{Al}_2\text{O}_3</math> or 70% <math>\text{Fe}_2\text{O}_3</math>.</p> <p><i>Condensation</i></p> <p>(1) Primary or secondary amines with acetylene:  Salts able to give ammoniates. Ammoniates on active substances.  <i>ZnBr}_2</i> on pumice.  <math>\text{Al}_2\text{O}_3</math> on silica gel.</p> <p>(2) Aromatic amines with acetylene:  Ammoniates precipitated on porous carriers.  Chlorides (<i>Al</i>, <i>Cu</i>, <i>Hg</i>).  <i>Hg</i> (chloride, bromide, iodic sulfate, nitrate).</p>
<p><i>Chlorination</i></p> <p><math>\text{Al}_2\text{O}_3</math> gel (grains).  Phosphates (<i>Fe</i>, <i>Al</i>, <i>Cd</i>, <i>Ce</i>).</p> <p><i>Condensation</i>  with acetylene:  Hydrolyzable metal halides, for example, <math>\text{BiCl}_3</math>.  Halogenated ethers, for example, chlormethyl ether.</p>	<p><i>f. Ethers.</i></p> <p><i>Decomposition</i></p> <p><i>Pt</i>.  <i>W</i>.  <math>\text{I}_2</math> and <math>\text{Cl}_2</math>.  <i>Sn</i> or <i>Zn</i> in the presence of acids.  <math>\text{SnCl}_4</math>.</p>	<p><i>Oxidation</i></p> <p><i>Cu</i>.  <i>Ag</i>.  Active charcoal.</p>
<p><i>Decomposition</i></p> <p><i>Zn</i>.  <i>Zn</i> chloride (anhydrous).  Hydroxides (<i>Zr</i>, <i>Th</i>).  Hydroxides (rare earths: <i>La</i>, <i>Ce</i>, <i>Pr</i>, <i>Nd</i>).  <i>Sa</i>, <i>I</i>.  <i>La</i> hydroxy gel.  <math>\text{Al}_2\text{O}_3</math>.  Acids: <math>\text{H}_2\text{SO}_4</math> on pumice.</p>	<p><i>g. Esters.</i></p> <p><i>Reduction</i></p> <p><i>Ni</i>.  <i>Ni</i> on kieselguhr.  <math>\text{Cu}</math> (2% by weight of the ester).  Mixtures:  <i>Cu</i> + <i>ZnO</i> on kieselguhr.  <i>Cu-Ba-Cr</i>.  <i>Cu-Ca-Cr</i>.  <i>CuO</i> on active <math>\text{Al}_2\text{O}_3</math> together with oxides (<i>Cr</i>, <i>Si</i>, <i>Ba</i>).  <i>CuO</i> on carriers (pumice, infusorial earth, silica gel).  Chromites (<i>Cu</i>, <i>Zn</i>, <i>Cd</i>).</p>	<p><i>Hydrogenation</i></p> <p><i>Ni</i>.  <math>\text{Ni}_2\text{O}_3</math>.  <i>Ni</i> on kieselguhr.  <i>Cu</i> (chromite, carbonate).  <math>\text{Cu-Cr}_2\text{O}_3</math>.</p>

Table 5. Groups of Catalysts Suitable for Reactions of Various Oils, Coal, Tar, and Wood.

## a. Oils.

<p><i>Oxidation</i></p> <p>(1) Fatty oils:  Borates (<i>Co</i>, <i>Mn</i>) (0.1–0.2%).  <i>Ni</i> and <i>Fe</i> salts.</p> <p>(2) Heavy oil:  <math>\text{AlCl}_3</math>.  Oxides (<i>Al</i>, <i>Ni</i>).</p> <p>(3) Solar oils:  Oxides (<i>Ti</i>, <i>V</i>, <i>Cr</i>, <i>Mn</i>, <i>Zr</i>, <i>Nb</i>, <i>Mo</i>, <i>Ta</i>, <i>W</i>, and <i>U</i>).  Acid salts (<i>Fe</i>, <i>Cu</i>, <i>Ni</i>, <i>La</i>, <i>Zn</i>, <i>Co</i>, <i>Th</i>, or rare earths).</p> <p>(4) Chinese wood oil:  <i>Co</i>, <i>Mn</i>, and <i>Pb</i> compounds (0.03–0.26%).</p> <p><i>Hydrogenation</i></p> <p><i>Ni</i>, <math>\text{Ni}_2\text{Cr}_2\text{O}_3</math>.  <i>Ni</i> (stearate, oxalate, carbonate, carbonyl, nitrate, silicate, tungstate, formate, acetate, propionate, butyrate, oleate, citrate).</p>	<p><i>Hydrogenation</i> (Continued)</p> <p>Mixtures:  <i>Ni</i> oxalate + <i>Al</i> nitrate.  <i>Ni</i> salt + <i>Na</i> aluminate on kieselguhr.  <i>Ni</i> nitrate + cane sugar solution (precipitated at 550–650° in a stream of <math>\text{CO}_2</math>).  <i>Ni</i> + <i>Mg</i> (<i>Al</i>) salts.  <i>Ni</i> on carriers (kieselguhr, fuller's earth, charcoal + kieselguhr).  <i>Ni</i> catalyst containing colloiddally dispersed charcoal.  <i>Ni</i> hydrate on charcoal.  Oxides (<i>Mo</i>, <i>Zn</i>, <i>Fe</i>, <i>Cr</i>).  Sulfides (<i>Mo</i>, <i>Co</i>, <i>W</i>, <i>Cr</i>, <i>Al</i>, <i>Fe</i>, <i>Cu</i>, <i>Ni</i>, <i>Sb</i>).  Iron oxides treated with mercaptans.  Chlorides (<i>Sn</i>, <i>Al</i>, <i>Fe</i>, <i>Zn</i>).  <math>\text{BF}_3</math>.  <i>Sb</i>-containing contacts are very active.  <i>Fe</i>, <i>Co</i>, <i>Ni</i>, <i>Ru</i>, <i>Rh</i>, <i>Pd</i>, <i>Os</i>, <i>Ir</i></p>	<p><i>Hydrogenation</i> (Continued)</p> <p>and/or <i>Pt</i> on carriers (kieselguhr, asbestos).  <i>Pt</i>, <i>Pd</i> on kieselguhr (1 part by weight in 10,000 parts of oil).  <i>Na</i> (for neutral oils).  Alkali aluminates.  Melts (<i>Sn</i>).  Mixtures:  <math>\text{MoS}_2</math> + <math>\text{MoO}_3</math> + <math>\text{Al}_2\text{O}_3</math>.  <math>\text{AlCl}_3</math> + phenol (equimolecular).</p> <p>(1) Fatty oils:  <i>Ni</i> (activated surface).  <i>Ni</i> on carriers (kieselguhr, japanese acid earth).  Mixtures:  <math>\text{Ni}(\text{NO}_3)_2</math> + <math>\text{Cr}(\text{NO}_3)_3</math>.  <i>Ni</i> (dispersed) + <i>Al</i> (obtained from an alloy).  <i>Sn</i>.  Double chromate of a nitrogen compound [<math>\text{NH}_3</math>, aniline, methylamine, pyridine and a hydrogenation metal (<i>Fe</i>, <i>Ni</i>, <i>Co</i>, <i>Cu</i>, <i>Sn</i>)].</p>
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Table 5 (Continued).

<i>Hydrogenation (Continued)</i>	<i>Hydrogenation (Continued)</i>	<i>Hydrogenation and Cracking (Continued)</i>
Active metal + organic acid (benzoic, oxalic, phthalic, or fatty acid).	(10) Camphor oil: Metallic layer on silica gel.	Fe <sub>2</sub> O <sub>3</sub> on cement. Sulfides (W). Alloys (Fe-Sn) (may contain Ni, Cr, Co). Mixtures. Compounds of organic acids soluble in oil or phenols with Mo, Zn, Cr, Co. Hydrogen compounds of As, Sb, Bi, B, Sn, or Si finely dispersed on CaO, BaO, active charcoal, asbestos, graphite. Mixture of H <sub>2</sub> and SiH <sub>4</sub> passed over Al <sub>2</sub> O <sub>3</sub> to form elementary Si. Charcoal paste: bauxite impregnated with 10% Cu + Zn (Cd). WS <sub>2</sub> + (B, Cr, Si, Ti, V, Mo, W, or Co).
(2) Mineral oils: Oxides (Fe, Co, W, V, Rh, Mo, Ni). Sulfides (W, Mo, V, Rh, Co, Ni). Iodine compounds with (As, Cu, Ti, Sn, Mn, Ni, or Co). Tungstates (NH <sub>3</sub> paratungstate). 70 parts NH <sub>3</sub> tungstate + H <sub>2</sub> S + 30 parts MoBr <sub>5</sub> . Alloys (of which the container is made). 13.8% Cr + 60.1% Ni + 13.8% Cr + 60.1% Ni + 24.2% Fe + 0.2% C. 25.0% Fe + 17.0% Cr + 58.0% Ni + 0.03% C.	(11) Turpentine oil: Benzene, toluene. (12) Heavy hydrocarbon oils: Oxides (Cr, Mo, W, V, Ti, Mn, Fe, Ni). Pt-Ni. Al-Fe (Cr <sub>2</sub> O <sub>3</sub> ). Mixtures: Halides (Fe, Zn, Sb) + organic compounds. AlCl <sub>3</sub> + hydrocarbons forming double compounds. Al <sub>2</sub> Cl <sub>6</sub> · C <sub>6</sub> H <sub>6</sub> . Mo. NH <sub>4</sub> MoO <sub>4</sub> (heated in O <sub>2</sub> then with Na <sub>2</sub> S + Na <sub>2</sub> S and CO <sub>2</sub> introduced). Cr + Mo compounds (together with Al, Zn or rare earths used in suspension). Oxides (Cr, Mo, W, V, Ti, Mn) + 5-20% Fe <sub>2</sub> O <sub>3</sub> + 10-70% SiO <sub>2</sub> + 5-50% oxides of alkaline earths. Alkali metals. Se and Ti (their compounds). Slag by refining. Fe alloys containing oxides (Cr, Mo, W). Adsorbents. Brown coal, pitch, solid coking residues.	<i>Desulfurization</i> Highly porous active substances (silica gel, bauxite, florida, fuller's earth). Ozone, air. Sulfides of the 6th group of the Periodic System, free from S and O compounds. Chlorides (Cu, Fe, Co, Hg, Cd). Nitrates (Cu, Hg). Hydroxides (Cu, Mg). MoO <sub>3</sub> · (NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> . Colloidal Mo acid (Na <sub>2</sub> Mo <sub>2</sub> S <sub>7</sub> (H <sub>2</sub> O) <sub>n</sub> on active charcoal). Fe (ores). Fe (sponge) (700-700°). Fe (sulfate, hydroxide, chloride). Metals of the Fe group or their mixtures or alloys: 40% Ni. Ni-Fe. NiO (CoO). Cu chromite. Mixtures: PbO and NaOH on 45-90% fuller's earth. MgO or Mg(OH) <sub>2</sub> + fuller's earth + oxidizing agent (Mn compound). 5% CuCl <sub>2</sub> + 5% KMnO <sub>4</sub> + 90% dry ton. 5% CuCl <sub>2</sub> + 1-8% HgCl <sub>2</sub> . (CoCl <sub>2</sub> , CdCl <sub>2</sub> ) + 95% ton. 1-30% CuCl <sub>2</sub> + remainder ton.
(3) Cottonseed oil: Ni. Ni (carbonate, nitrate). Co, Fe, Cu. Pt. Contact containing permuto-genetic body.	(13) High boiling oils converted into low boiling oils. Finely divided metals (Ni, Pd). Fe filings. Oxides (Th, Zn, Fe). Oxides (Mg, Mo). Sulfides (Mo, W, Cr, U, Re) alone or together with basic substances (pyridine bases, NH <sub>3</sub> , or alkalis K <sub>2</sub> CO <sub>3</sub> , LiCO <sub>3</sub> , etc.). AlCl <sub>3</sub> .	
(4) Castor oil: Oxides, sulfides, phosphates, or silicates of (Al, W, Zr, Mo, U). WO <sub>3</sub> (0.5-1%). Ni-Cu (80-90 at. % Ni + 10-20 at. % Ni). Pd-Co (8.5% : 15%).		
(5) Sunflower oil: Ni.		
(6) Olive oil: Colloidal Pt + 0.1% saponin.		
(7) Fish oil: Ni, Fe, Co.		
(8) Nut oil: Ti, U, Mn, V, Ni, Ta.		
(9) Phenolic oil: Oxides (Ni, Mo, Fe, Al). NiO and I <sub>2</sub> . Chlorides (Sn) less active.	<i>Hydrogenation and Cracking</i> Finely dispersed hydrogenation catalysts. Oxides (Mn, Al, Fe, Zn, Sn, Co, Ni, Cr). Mo-Zn. MoO <sub>3</sub> -ZnO.	

## b. Coal.

*Hydrogenation*  
Mo (reduced at 400°).  
Mo oxides (readily reduced).  
Mo sulfide.  
Mo (or compounds) together with oxides.  
Molybdic acid (0.2%) in CH<sub>3</sub>OH.  
W or Cr with oxides (Al, Mg, Zn, Cr) as activators.  
Fe (at 500°).  
Fe<sub>2</sub>O<sub>3</sub>.  
Fe<sub>3</sub>O<sub>4</sub> (slightly reduced).  
Fe<sub>2</sub>O<sub>3</sub> (5%).  
FeS<sub>2</sub>, CaO and SiO<sub>2</sub> added in an amount equal to the ash content.  
FeS<sub>2</sub> (precipitated from FeCl<sub>3</sub> by (NH<sub>4</sub>)<sub>2</sub>S).  
Hydrated iron oxide (5%).  
Globules of Fe (Zn).  
Soluble compounds of Fe (Co) or both.  
Halides or sulfates with finely dispersed Fe (sponge Fe or Fe carbonyl treated with alkali).

*Hydrogenation (Continued)*  
Sn (melted).  
Sn (oxalate, oxyhydrate) used with solvents (tetralene, phenol, pyridine).  
Na aluminate.  
Na (K) compounds combined with Al, Fe, Sn.  
Chlorides (AlCl<sub>3</sub>, CCl<sub>4</sub>, CHCl<sub>3</sub>, CHBr, CHCl<sub>3</sub>).  
Halide derivatives of benzene and NH<sub>4</sub>Cl.  
Acids (hydroiodic, sulfuric, acetic, amino).  
Mineral ingredients of coal.

*Pressure Hydrogenation*

Fe.  
Active Fe precipitated on infusorial earth.  
Mixtures:  
85% Fe + 15% Zn.  
Fe(Ni, Cu, Co, Mn, Cr, Mo, Sn, Al) + alkalis or alkaline earths + Si or B.

*Pressure Hydrogenation (Continued)*  
Fe oxide containing Ti (as obtained in the production of bauxite).  
Mixtures of metallic Fe, Fe (oxides, hydrates), natural or artificial limonite or bauxite residues (iron content calculated as Fe<sub>2</sub>O<sub>3</sub> (50-60%).  
Fe (Mn, Cu) sulfides, phosphides + phosphates (Mo, Sn, W) or chlorides (Ni, Mn) or alkali borates.  
Mo.  
Mo + activators (Si, B, Li, P, Ce, also H<sub>2</sub>S or substances producing it).  
Heteropolymer acids containing Mo:  
(NH<sub>4</sub>)<sub>2</sub>Mo<sub>10</sub>O<sub>31</sub> · 3H<sub>2</sub>O.  
NH<sub>4</sub> pentaecamolylbdate.  
(NH<sub>4</sub>)<sub>2</sub>(MoO<sub>4</sub> · 6H<sub>2</sub>O)<sub>11</sub>.  
(NH<sub>4</sub>)<sub>2</sub>PO<sub>4</sub>(MoO<sub>4</sub> · 6H<sub>2</sub>O)<sub>11</sub>.  
NH<sub>4</sub> silico molybdate.

Table 5 (Continued).

Pressure Hydrogenation (Continued)	Pressure Hydrogenation (Continued)	Pressure Hydrogenation (Continued)
<p><math>\text{NH}_4</math> tungsten molybdate.</p> <p><math>\text{NH}_4</math> chromium molybdate.</p> <p><math>\text{NH}_4</math> aluminum molybdate (more active than simple Mo compounds, such as <math>\text{MoO}_3</math>).</p> <p><math>\text{MoO}_3</math> (treated with <math>\text{H}_2</math> for 15 hours at <math>230^\circ</math> gives pseudomorphous (<math>\text{MoO}_2</math>)).</p> <p><math>\text{MoO}_2</math>.</p> <p><math>(\text{NH}_4)_2\text{MoO}_4</math> (0.1% <math>\text{MoO}_3</math> on charcoal).</p> <p>0.1% <math>\text{MoO}_3</math> adsorbed in the form of ferridac earth impregnated with <math>(\text{NH}_4)_2\text{MoO}_4</math> in the ratio 4 : 1.</p> <p><math>\text{MoS}_2</math>.</p> <p>Mo halide (with <math>\text{I}_2</math> compounds of Ag, Cu, Ti, Sn, Mn, Ni and Co) on active charcoal, silica gel, or pumice.</p> <p>Mo-Cr.</p> <p>Al molybdate.</p> <p>Mo on ceramic mass.</p> <p>Mixtures:</p> <p><math>\text{MoS}_3</math> + boron sulfide.</p> <p>Acid salts of Mo (Sn) + acids (formic, oxalic, acetic).</p> <p>Mo oxides or sulfide mixed with oxides (Zn, Mg).</p> <p><math>\text{MoS}_2</math> mixed with strong primary or secondary bases (cyclohexylamine, piperidine, or octadecylamine serve as solvents) + a small amount of S.</p>	<p>Mo solution impregnated on charcoal mixed with a wetting agent (isopropyl naphthalene), sulfonic acid is added to the solution.</p> <p>Strong catalysts (Mo, Sn, W, Re, U, V, Cr, Ni, Co) mixed with weak catalysts such as sulfides, phosphides, phosphates (Mn, Fe, Cu).</p> <p>W (oxides, sulfides).</p> <p>W on ceramic mass (pseudo-morphous).</p> <p>W (monoclinic needles of ammonium paratungstate treated with <math>\text{H}_2\text{S}</math> for 48 hours at <math>300^\circ</math>).</p> <p>W sulfide (treated under 200 atm.).</p> <p><math>\text{WS}_2</math> on active charcoal or silica gel.</p> <p>W dissolved in cyclohexylamine, piperidine, ammonium tungstate.</p> <p>Mixtures:</p> <p>W oxides or sulfides mixed with oxides (Zn, Mg).</p> <p><math>\text{NH}_4</math> tungstate mixed with <math>\text{HNO}_3</math> and precipitated with an excess 1-4% free <math>\text{H}_3\text{PO}_4</math>.</p> <p><math>\text{NH}_4</math> sulfo tungstate mixed with <math>\text{TiCl}_4</math> in benzene.</p> <p>5% <math>\text{NH}_4</math> sulfo tungstate + 1 mol <math>\text{CoCl}_2</math>.</p>	<p><math>\text{NH}_4</math> sulfo tungstate + <math>\text{FeSO}_4</math>. 2 parts <math>\text{WS}_2</math> + 1 part <math>\text{NiS}_2</math>.</p> <p>W (oxide or sulfide) + Pd (oxide sulfide, chromate, acetate).</p> <p>Acid sulfates of W (Mo) + Pb salts (hydroxide, oxide, chromate).</p> <p>W compound soluble in <math>\text{H}_2\text{SO}_4</math> + isopropyl naphthalene sulfonic acid (impregnated).</p> <p>Sn (organic compounds: oxalates, acetates, formates, tetraphenyl).</p> <p>Mixtures:</p> <p>Sn + alkalis or alkaline earths.</p> <p>Acid salts of Sn + Si, B, or oxalic, acetic acids.</p> <p>Zn (dust + <math>\text{NaOH}</math>).</p> <p>Zn + Ni (alloy, equal parts).</p> <p>ZnO (MgO) pretreated with <math>\text{H}_2\text{S}</math>.</p> <p>Zn (butyrate, acetate, propionate).</p> <p>ZnO (MgO) + oxides or sulfides (Cr, Mo, W).</p> <p>Ag on magnesite or magnesite.</p> <p>Ag-Cu.</p> <p>Ag-Cr (Fe).</p> <p>Rh.</p> <p>Rh (oxide, sulfide) on charcoal.</p> <p>Rh compounds in colloidal state.</p> <p>Pd (oxide, sulfide, chromate) on carriers.</p>

## c. Tar and Wood.

Tar	Wood
<p>Hydrogenation</p> <p>Mo (in the presence of <math>\text{H}_2\text{S}</math>).</p> <p><math>\text{MoO}_3</math> (<math>300^\circ</math>, 180 atm.).</p> <p><math>\text{H}_2\text{MoO}_4</math>; <math>(\text{NH}_4)_2\text{MoO}_4</math> (1%).</p> <p>Mixtures:</p> <p><math>\text{MoO}_3</math> + CuO.</p> <p><math>\text{MoO}_3</math> + S.</p> <p><math>\text{MoO}_3</math> + <math>\text{Cr}_2\text{O}_3</math> + kaolin.</p> <p><math>\text{MoO}_3</math> + ZnO.</p> <p>Na (hydride, formate).</p> <p>Fe sulfide.</p> <p>Ni oxide.</p> <p>Pt, Pd, Ni, Co.</p> <p>Halides (S, Se, Te, B, P).</p>	<p>Hydrogenation</p> <p><math>\text{Fe}</math>, Co, Ni, Cu.</p> <p>Oxides (<math>\text{Fe}</math>, Co, Ni, Cu).</p> <p>Oxides or hydroxides or metal compounds not readily reduced under conditions of the reaction.</p>

## d. Destructive Hydrogenation of Hydrocarbons.

<p>Mixtures:</p> <p><math>\text{MoO}_3</math> + <math>\text{SiO}_2</math> (heated at <math>300</math>–<math>600^\circ</math> in non-reducing gases (<math>\text{CO}_2</math>, <math>\text{SO}_2</math>, NO, <math>\text{O}_2</math>, air, <math>\text{N}_2</math>)).</p> <p><math>\text{MoO}_3</math> + oxides (Zn, Al, Mg).</p> <p>Mo-Cr.</p> <p><math>\text{MoS}_2</math> (finely dispersed on active charcoal).</p> <p><math>\text{MoS}_2</math>.</p> <p>Mo polysulfide on charcoal.</p> <p><math>(\text{NH}_4)_2\text{WS}_4</math> (<math>425^\circ</math>).</p>	<p>Sn (oxalate, formate, acetate).</p> <p>Sn tetraphenyl + oxides (Cu, Fe).</p> <p>Ti compounds.</p> <p>Cr.</p> <p>5.5% Cr + 1.6% Ni + 0.1% C.</p> <p><math>\text{Cr}_2\text{O}_3</math> + MgO (equimolecular amounts) with an aqueous solution of <math>\text{CrO}_3</math>.</p> <p>0.2% <math>\text{PbCl}_2</math> + oil (1 : 1) + 0.8% <math>\text{CCl}_4</math> or halides (P, S, Se, As, Sb).</p>
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## PART II

## Catalytic Synthesis in Inorganic Chemistry

Table 1. Catalytic Synthesis of Hydrogen and Oxygen.

Reaction	Catalyst	Observer
Synthesis of $\text{H}_2\text{O}$ ; the activation of $\text{O}_2$ , not of $\text{H}_2$ , plays a dominating part in catalysis; intensive oxidation and reduction of the catalyst is equivalent to catalytic formation of water.	Ni prepared by reduction at $400^\circ$ .	Benton and Emmett: <i>J. Am. Chem. Soc.</i> , <b>48</b> , 632-40 (1926).
Synthesis of $\text{H}_2\text{O}$ from detonating gas (chain mechanism assumed); T. $50-60^\circ$ ; reduction occurs only upon the catalyst surface activated by adsorbed $\text{H}_2$ .	Pt black; $\text{WO}_3$ reduced to $\text{W}_2\text{O}_3$ in the presence of Pt (intimate mixing of $\text{WO}_3$ and Pt).	Foresti: <i>Ateneo parmense</i> , <b>4</b> , 805-12 (1932); refer also to Kobosew and Anochin: (Refer to C. 1931 II 673); <i>Z. physik. Chem. (B)</i> , <b>13</b> , 63-71 (1931).
Synthesis of $\text{H}_2$ and $\text{O}_2$ ; long "induction interval" makes the catalyst active; $\text{H}_2$ hinders reaction, while $\text{O}_2$ accelerates it. (kinetic measurements reveal the mechanism: alternate oxidation of Pd and reduction of the oxide).	Pd (similar to catalysis with Ni and Ag).	Chapman and Gregory: <i>Proc. Roy. Soc. London (A)</i> , <b>147</b> , 68-75 (1934); refer also to de La Rive and Marcet: <i>Ann. chim. phys.</i> , <b>39</b> , 328 (1828).
Synthesis of $\text{H}_2$ and $\text{O}_2$ .	Pt (becomes inactive if heated at $1000^\circ$ in $\text{H}_2$ and then in $\text{O}_2$ ) (only through very long oxidizing, heating and open mordant action of $\text{HCl}$ may it be activated; the inactivation is ascribed to the fact that $\text{CuO}$ present in small amounts in all Pt is reduced to metal on heating in $\text{H}_2$ , and through diffusion reaches the surface and is oxidized by heating in $\text{O}_2$ , whereby Pt is covered with an inactive layer; experiments with Pt covered with small amounts of Cu confirmed this assumption; the activity reduction effect was small in the case of specially purified Pt containing 0.001% impurities).	Chapman and Reynolds: <i>Proc. Roy. Soc. London (A)</i> , <b>156</b> , 284-306 (1936).
Synthesis of $\text{H}_2$ and $\text{O}_2$ to form water; $\text{H}_2 : \text{O}_2 = 2 : 1$ ; 1 : 1 and 4 : 1; T. $170-250^\circ$ ; (1) reaction consists in activated diffusion of $\text{H}_2$ ; (2) reaction consists in activated diffusion of $\text{O}_2$ into Cu; the catalytic water formation itself takes place on the oxidized surface with an activation energy of 9 k. cal.; it is possible that activated diffusion of $\text{O}_2$ leads to the formation of $\text{Cu}_2\text{O}$ and a free Cu atom from $\text{CuO}$ ; Cu or any other metal which is not poisoned by $\text{O}_2$ is available for the chemisorption of $\text{H}_2$ .	Cu and Cu-Au alloy.	van Cleave and Rideal: <i>Trans. Faraday Soc.</i> , <b>33</b> , 635-643 (1937).
Synthesis of $\text{H}_2$ and $\text{O}_2$ or combustion of $\text{H}_2$ ; a reduction of $\text{CuO}$ to $\text{Cu}_2\text{O}$ assumed to precede; the catalytic action by van Cleave and Rideal is considered wrong; $\text{CuO}$ is ascertained to be unchanged and formation of active centers from $\text{Cu}_2\text{O}$ is improbable.	$\text{CuO}$ .	Fedeschi: <i>Gazz. chim. ital.</i> , <b>67</b> , 609-611 (1937).

Table 2. Catalytic Synthesis of Hydrogen and Iodine or Bromine Vapor.

Reaction	Catalyst	Observer
Synthesis of $H_2$ and $I_2$ vapor followed by dissociation of HI at the same temperature.	Pt sponge.	Corenwinder: <i>Ann. chim. phys.</i> (3), 34, 97 (1852). Hautefeuille: <i>Compt. rend.</i> , 64, 608 (1867).
Synthesis of HBr from $H_2$ and $Br_2$ .	Sugar coal 80% burned shows maximum catalytic activity and the adsorption ability reaches a maximum when 35% burned; the decrease in catalytic activity, as well as in the adsorption ability by strong burning, is ascribed to the decrease in the total surface by burning of small graphite crystals; the activation heat of the reaction $H_2 + Br_2$ does not depend on the burning extent; on the average for all investigated kinds of coal it is 30,000 cal.	Bruns and Zarubina: <i>Ada Physicochim. U.R.S.S.</i> , 8, 787-794 (1938).

Table 3. Catalytic Synthesis of Hydrogen Cyanide.

Reaction	Catalyst	Observer
$CO + NH_3 \rightarrow HCN + H_2O$ .	Alkalized charcoal; glassy $Al_2O_3 + ThO_2$ and other oxide additions, Zr, U.	Gold- und Silberscheideanstalt: E.P. 242,685 (1924). I. G. Farbenindustrie A.-G.: E.P. 220,771 (1923).
$CO + NH_3 \rightarrow HCN + H_2O$ .	$Fe_2O_3 + Na_2O$ .	Eichwald: F.P. 595,399 (1924).
$CO + NH_3 \rightarrow HCN + H_2O$ .	Oxides of Ce, Ti, Ca or their mixtures with oxides of Al, Th, Ti, Zr on carbides or silicides as carriers.	Bredig and Elöd: Swiss P. 111,726 (1926).
$HCO \cdot NH_2 \rightarrow HCN + H_2O$ (industrial process).	Fe, Mn, Ni, Al, Cu.	I. G. Farbenindustrie A.-G.: E.P. 269,166 (1927).
Synthesis of HCN from formamide by evaporation; T. 250-400°; directly afterward brought in contact with (2); T. 450-700°.	(1) $Al_2O_3$ , $SiO_2$ -Si or Carborundum powder. (2) Mn, Al, Mg, Cr as well as melted oxides of these metals.	E. I. Du Pont de Nemours & Co., Inc.: E.P. 469,563, Aug. 26, 1937. Refer also to U.S.P. 2,042,451 (1936).
Synthesis of CO and $NH_3$ to HCN as well as formamide (industrial process).	The reaction proceeds in a zone where no Fe metal is present, e.g., Cu, brass, Al used.	Badische Anilin- und Soda Fabrik: (1924/1925).
Synthesis of HCN from formamide; T. 400-700°.	Pieces or grains of $MnO$ ; better in a melted or sintered form.	E. I. Du Pont de Nemours & Co., Inc.: (Larson): E.P. 470,406, Sept. 9, 1937.
Production of HCN; T. 500-700°. $2CO + NH_3 \rightarrow HCN + CO_2 + H_2$ $CO_2 + H_2 \rightarrow CO + H_2O$ side reactions: $2CO \rightarrow C + CO_2$ $C + NH_3 \rightarrow HCN + H_2$ .	Al or Ce deposited on alumina.	Bredig, Elöd and Muller: <i>Z. Elektroch.</i> , 36, 1003, 1007 (1930).
Production of HCN from $NH_3$ and CO taken in a ratio 1 : 0 : 9 : 4; T. 570°.	Catalyst prepared by adding conc. $NH_3$ to a solution of Al nitrate and treating the dried precipitate with a solution of Zr salt.	Fuchs and Verbeck: <i>Ind. Eng. Chem.</i> , 27, 410 (1935).
Production of HCN from $NH_3$ passed through $CaH_2$ in a ratio 6 : 1, T. 28° or through toluene in a ratio 7 : 1, T. 50-55°.	Kieselguhr impregnated with alumina at 1100-1150°.	Fulton and Koppers Co. (Dela-ware): U.S.P. 1,872,923 (1933).
Production of HCN from $NH_3$ , air and $CH_4$ in volumetric ratio, 2 : 14 : 4 : 2; T. 1000°; $CH_4$ is said to combine with "nitroxyl," the primary product of oxidation of $NH_3$ to HCN; 60% $NH_3$ recovered as HCN and 10% lost as nitrogen; the remainder remains unchanged.	Pt gauze.	Andrussow: <i>Angew. Chem.</i> , 48, 593 (1935).



Table 4. Catalytic Synthesis of Ammonia.

Reaction	Catalyst	Observer
High-pressure synthesis of $\text{NH}_3$ .	Fe.	Haber (1908) carried out on an industrial scale (1910-1914).
Synthesis of ammonia: $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ (source of the gas mixture 25% $\text{N}_2$ and 75% $\text{H}_2$ derived from coke or lignite); T. 550-600°; pressure, 220 atm.; yield of $\text{NH}_3$ , 8% at each passage; the conversion of $\text{N}_2$ - $\text{H}_2$ mixture into $\text{NH}_3$ is relatively high at pressures of about 1000 atm., although 100 atm. pressure is about enough for the commercial process at 600°.	Fe; in the absence of catalysts the attainment of an equilibrium is exceedingly slow even at high temperatures, such as 800-1000°.	Haber: <i>Z. anorg. allgem. Chem.</i> , <b>43</b> , 111 (1905). Haber and Le Rossignol: <i>Z. Elektrochem.</i> , <b>14</b> , 181 (1908). Haber and Le Rossignol: <i>Ibid.</i> , <b>19</b> , 53 (1913). Haber and Greenwood: <i>Ibid.</i> , <b>20</b> , 297 (1914). Haber and Greenwood: <i>Ibid.</i> , <b>21</b> , 241 (1915); Refer also to Stroug: <i>Ind. Eng. Chem.</i> , <b>3</b> , 403 (1927).
Synthesis of $\text{NH}_3$ .	$\text{Al}_2\text{O}_3$ +alkalies.	Badische Anilin- und Soda Fabrik: G.P. 249, 447 (1910).
Synthesis of ammonia: ( $\text{H}_2$ obtained from coke-oven gas, electrolytic $\text{H}_2$ , or from water gas); 900-1000 atm. pressure.	Peroxidized Fe; as appropriate catalysts are considered those active from 400° and upwards.	Claude Process: E.P. 130,086 (1918). E.P. 131,870 (1919). E.P. 161,195 (1921). Refer also to <i>Bull. soc. chim.</i> , <b>27</b> , 705 (1920). <i>Chimie &amp; industrie</i> , <b>4</b> , 5 (1920). <i>Z. angew. Chem.</i> , <b>43</b> , 417 (1930).
Synthesis of $\text{NH}_3$ .	$\text{K}_2\text{Mn}(\text{CN})_6$ . $\text{Ba}_2\text{Mn}(\text{CN})_{10}$ .	Norsk Hydro-Elektro.: F.P. 525,504, Sept. 23, 1921.
Synthesis of $\text{NH}_3$ .	$\text{Fe}_2\text{O}_3$ .	Razous: <i>Ind. chim. belge.</i> , <b>8</b> , 135-158 and 213-216 (1921).
Synthesis of $\text{NH}_3$ .	Double compounds of cyanide $\text{CoCaFe}(\text{CN})_6$ .	Norsk Hydro-Elektro.: F.P. 525,504, Sept. 23, 1921.
Synthesis of $\text{NH}_3$ .	Alkali or alkaline earths, cyanamide+Co, Os, V, Ti.	E.P. 140,439, Oct. 20, 1921.
Synthesis of $\text{NH}_3$ .	Pyrophoric Fe (from Fe oxalate).	Norsk Hydro-Elektro.: E.P. 171,976, Jan. 18, 1922.
Synthesis of $\text{NH}_3$ .	$\text{MnCO}_3$ , Co acetate.	Clancy: E.P. 179,155, June 28, 1922.
Synthesis of $\text{NH}_3$ .	Pt, Os, or Ni.	Weintraub: G.P. 354,212, Kl 12g, June 1, 1922. F.P. 532,343, Feb. 1, 1922.
Synthesis of $\text{NH}_3$ .	Fe oxalate.	Clancy: E.P. 179,155, June 28, 1922.
Synthesis of $\text{NH}_3$ .	$\text{Al}_2\text{O}_3$ , $\text{MgO}$ , $\text{CaO}$ +Pb, Cd, Bi, or Zn.	Urfer: E.P. 199,032, Aug. 9, 1923.
Synthesis of $\text{NH}_3$ .	Ferrous or ferric salts of Ca, Ba, Mg, Mn.	Synthetic Ammonia and Nitrates Ltd.: E.P. 237,394, Aug. 21, 1925.
Synthesis of $\text{NH}_3$ .	Thermo-ionic emission from Fe alkali contacts.	Kunsman: <i>Proc. Nat. Acad. Sci. U. S.</i> , <b>12</b> , 659-662 (1926); <i>J. Franklin Inst.</i> , <b>203</b> , 635-646 (1926).
Synthesis of $\text{NH}_3$ .	Pure Fe and activated Fe (from $\text{Fe}_3\text{O}_4$ ).	Almquist and Crittenden: <i>Ind. Eng. Chem.</i> , <b>18</b> , 1307-1309 (1926).
Synthesis of $\text{NH}_3$ .	Fe oxides+substances of high combustion heat and not readily reducible metal oxides.	Casale: Can. P. 265,074, Feb. 19, 1926.
Synthesis of $\text{NH}_3$ .	Fe (heat of adsorption, 16 calories).	Daw and Taylor: <i>J. Phys. Chem.</i> , <b>31</b> , 277-290 (1927).
Synthesis of $\text{NH}_3$ .	Complex Fe cyanide.	Mittasch, Kiss and Emmett: <i>Z. anorg. allgem. Chem.</i> , <b>170</b> , 193-212 (1927).

Table 4 (Continued).

Reaction	Catalyst	Observer
Synthesis of $\text{NH}_3$ ; (N taken from residual gases obtained from nitric acid; hydrogen obtained electrolytically); T. about $600^\circ$ ; pressure 300-500 atm.	Platinized asbestos.	Fausser: U.S.P. 1,487,647 (1924). E.P. 240,436 (1925). E.P. 295,129 (1928). E.P. 313,446 (1929).
Synthesis of $\text{NH}_3$ ; (nitrogen obtained by burning oxygen of the air with $\text{H}_2$ and water formed condensed and electrolyzed to obtain $\text{H}_2$ ).	Platinized asbestos.	Casale: E.P. 176,144 (1920). E.P. 185,179 (1921). E.P. 193,789 (1922). E.P. 197,199 (1922). E.P. 231,417 (1924). U.S.P. 1,408,987 (1922). U.S.P. 1,447,123 (1923).
Synthesis of $\text{NH}_3$ ; T. $400^\circ$ ; pressure 100 atm.	Complex ferrocyanides, such as K-Al ferrocyanide in acetanhydride solvent.	Mont-Cenis (Uhde Process): E.P. 247,225 (1925). E.P. 247,226 (1925). E.P. 253,122 (1925). E.P. 259,230 (1925). E.P. 272,930 (1926). Can. P. 283,221, Sept. 11, 1928.
Synthesis of $\text{NH}_3$ .	Tablets of Fe oxide (pressure used for pressing 800-1100 kg.).	Schultze: Dutch P. 16,147, April 16, 1927.
Synthesis of $\text{NH}_3$ .	Fe + alkaline earths + Al.	Uhde: E.P. 273,933, Aug. 31, 1927.
Synthesis of $\text{NH}_3$ .	$\text{Fe}_2\text{O}_3 + \text{MnO}_2$ (mixed with Al reducing in weight ratio 0.19 : 7.24 : 0.07 the oxides with development causing the metal to melt).	Read: U.S.P. 1,618,004, Feb. 15, 1927.
Synthesis of $\text{NH}_3$ .	Fe oxides + $\text{K}_2\text{O}$ and $\text{MgO}$ ; $\text{Fe}_3\text{O}_4$ + small amount of HF.	Lazota, Inc.: U.S.P. 1,667,322, April 14, 1928.
Synthesis of $\text{NH}_3$ .	Alkaline earths or metal salt of Fe + $\text{ZrO}_2$ .	Huster: E.P. 305,753, March 7, 1929.
Synthesis of $\text{NH}_3$ .	$\text{Si}(\text{OH})_4$ gel impregnated with $\text{Ni}(\text{NO}_3)_2 + \text{Fe}(\text{NO}_3)_3 + (\text{AlNO}_3)_3$ ; $\text{Si}(\text{OH})_4$ gel impregnated with $\text{K}_2\text{CO}_3$ (10 N).	Marconi: Ital. P. 276,011, Jan. 26, 1929.
Synthesis of $\text{NH}_3$ .	Porous carrier + alkali Fe cyanide.	Clancy: U.S.P. 1,363,393, Dec. 28, 1930.
Synthesis of $\text{NH}_3$ .	Fe + Al; Os + alkali metal.	Mittasch: <i>Z. Elektroch.</i> , <b>36</b> , 569-580 (1930).
Synthesis of $\text{NH}_3$ .	Ni + Mo.	Reuncke: <i>Ibid.</i> , <b>36</b> , 190-192 (1930).
Synthesis of $\text{NH}_3$ .	Fe + Mo + W (Fe precipitated with NaCl on a wire net of Mo-W or Pt).	I. G. Farbenindustrie A.-G.: F.P. 694,076, Nov. 28, 1930.
Synthesis of $\text{NH}_3$ .	Pt wire nets of various mesh width (the narrow meshes are exposed to current cells, while the wide meshes are exposed to the washing gas).	Azogeno Soc. Anon. Fabricazione della Ammoniaea: E.P. 337,680, Nov. 27, 1930.
Synthesis of $\text{NH}_3$ .	Fe + As, B, P (small amounts or their compounds melted in an $\text{O}_2$ stream).	Gesellschaft für Chemische Industrie: E.P. 359,378, Nov. 12, 1931.
Synthesis of $\text{NH}_3$ .	$\text{K}_3\text{Fe}(\text{CN})_6 + \text{KCl}$ . $\text{AlFe}(\text{CN})_6$ .	Patentverwertung A.-G. (Alpina. Société Anonyme pour l'Exp. des Brevets): Swedish P. 72,689, Sept. 22, 1931.
Synthesis of $\text{NH}_3$ .	Os + K (vapor).	I. G. Farbenindustrie A.-G.: F.P. 707,577, July 9, 1931. E.P. 353,622, Aug. 20, 1931.
Synthesis of $\text{NH}_3$ .	Alkali or alkaline-earth salts of Fe cyanide treated with strong acids ( $\text{HCl}$ , $\text{H}_2\text{SO}_4$ , $\text{HI}$ , $\text{H}_3\text{PO}_4$ ).	Dutch P. 28,442, Dec. 15, 1932.

Table 4 (Continued).

Reaction	Catalyst	Observer
Synthesis of $\text{NH}_3$ .	Metal-N mixed crystals: (1) Ta-N (solid solution). (2) U-N heat of formation: (1) = $58 \pm 1$ k. cal. (2) = $68.5$ k. cal./g. N.	Kröger: <i>Z. Elektroch.</i> , <b>39</b> , 670-71 (1933).
Synthesis of $\text{NH}_3$ .	Fe carbide (sulfur compounds increase stability).	Müller: E.P. 271,482, July 13, 1927. Boehringer und Sohn A.-G.: G.P. 582,435, Aug. 15, 1933.
Synthesis of $\text{NH}_3$ .	Base exchange mixture (without Si contact) + Fe.	Selden Co. (Jaeger): U.S.P. 1,926,099, Sept. 12, 1933.
Synthesis of $\text{NH}_3$ .	Uranium-containing nitrogen according to the relation: $\text{UN}_2 + \text{N}_2 = \text{UN}_{(2.25)}$ ; analogous relations are supposed (pure metal is not active, only the one containing nitrogen); in case of Fe and Os metals, the presence of N in them is not necessary.	Frankenburger: <i>Z. Elektroch.</i> , <b>39</b> , 269-81 (1933); <b>39</b> , 818-20 (1933).
Synthesis of $\text{NH}_3$ .	Kunsman's catalyst (activity ascribed to the presence of alkalis).	Powell and Brate: <i>Nature</i> , <b>131</b> , 168-169 (1933); refer also to Pease and Taylor: <i>J. Phys. Chem.</i> , <b>24</b> , 241-64 (1920). Larson, Newton and Hawkins: <i>Chem. &amp; Met. Eng.</i> , <b>26</b> , 493-97 (1922). Rideal: <i>Mon. sci.</i> (5), <b>12</b> , 3-9, 73-83 (1922). Taylor: <i>Ind. Eng. Chem.</i> , <b>18</b> , 958-60 (1926). Valentin: <i>Z. physik. Chem.</i> , <b>40</b> , 271-72 (1927). Norsk Hydro-Elektro.: Norweg. P. 437,786, March 7, 1927.
Synthesis of $\text{NH}_3$ ; (the non-catalytic pure thermal synthesis of $\text{NH}_3$ is practically impossible because of the relatively high activation energy required from the $\text{N}_2$ molecule) (it is estimated for the maximum 210 k. cal. and for the minimum of more than 55 k. cal.).	Active catalysts are metals belonging to the transition elements, which have underneath the external shell a partially unoccupied electronic level and therefore show a tendency for electron exchange; the choice within the group of transition elements is determined by the requirement of a smaller stability of intermediate products formed; likewise the heat of formation as well as the heat of activation of their conversion in $\text{NH}_3$ formation must be small, i.e., less than about 30-40 k. cal. (V and Ta, for example, as result of too high a heat of formation of their nitrides are excluded as catalysts in synthesis of ammonia); important factors for the reactivity are distance relations of atoms, atomic groups and molecules, i.e., the steric state of reaction components quantitatively measured by Polanyi; the use of a catalyst avoids application of a high activation energy by introducing intermediate reactions with the catalyst, either by subdividing the activation energy in partial amounts and stepwise addition of the activation energy, or by a summary decrease of the activation energy required brutto; for the majority of catalytic conversions the 2nd mechanism is assumed.	Frankenburger: <i>Z. Elektroch.</i> , <b>39</b> , 269-281 (1933); refer also to Hagg: (Refer to C. 1931 II 675, 816); <i>Z. physik. Chem.</i> (B), <b>12</b> , 33 (1931). Eyring and Polanyi: (Refer to C. 1931 I 3433); <i>Z. physik. Chem.</i> (A), <b>12</b> , 279 (1931). Polanyi: (Refer to C. 1932 II 1622 and 3261).

Table 4 (Continued).

Reaction	Catalyst	Observer
Synthesis of $\text{NH}_3$ ; the activated adsorption of nitrogen is the rate-determining step.		Emmett and Brunaker: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 35 (1934).
Synthesis of $\text{NH}_3$ ; on the basis of thermo-dynamic and kinetic relationships it is deduced that the reaction is a monomolecular one and that it may be expressed by an equation derived for $\alpha$ -concentration of $\text{NH}_3$ and $t$ , time of the reaction, in the form: $\alpha = (e^{kt} - 1)Q / (e^{kt} + Q)$ wherein $Q$ is the theoretical equilibrium concentration.		Popowitsch: <i>Khimstroj</i> , <b>6</b> , 258-266 (1934).
Synthesis of $\text{NH}_3$ .	Fe; $\text{Al}_2\text{O}_3$ , $\text{MgO}$ and $\text{SiO}_2$ increase activity, but not the stability; $\text{K}_2\text{O}$ increases stability but slightly decreases the yield of $\text{NH}_3$ ; $\text{K}_2\text{O} + \text{Al}_2\text{O}_3$ increases activity and stability; $\text{MgO} + \text{SiO}_2$ gives greater stability used as a mixture than when used singly; $\text{MgO}$ and $\text{K}_2\text{O} + \text{Al}_2\text{O}_3$ up to a certain limit are practically without influence upon the activity of the catalyst and the yield, but increase the stability.	Latschinow and Telegin: <i>Zhur. Khim. Prom.</i> , <b>12</b> , 31-33 (1934).
Synthesis of $\text{NH}_3$ .	Ti magnetite less sensitive to poisons than Fe activated with Al and K; 0.01-0.1 vol. % of $\text{O}_2$ poison; 0.02-0.1 vol. % CO poison.	Epstein and Upolownikow: <i>Ibid.</i> , <b>10</b> , 37-39 (1934).
Synthesis of $\text{NH}_3$ .	Dispersion of Fe with NaCl.	Dobytschin and Frost: <i>Z. Elektroch.</i> , <b>40</b> , 585-87 (1934).
Synthesis of $\text{NH}_3$ .	Fe + Mo.	Finkelstein: <i>Acta Physicochim. U.R.S.S.</i> , <b>1</b> , 521-524 (1934).
Synthesis of $\text{NH}_3$ .	Ti magnetite + Fe cyanide (Ti magnetite equivalent in catalytic activity to Fe oxide).	Epstein and Upolownikow: <i>Zhur. Khim. Prom.</i> , <b>10</b> , 41-44 (1933); <b>12</b> , 37-39 (1934).
Synthesis of $\text{NH}_3$ .	Fe or Fe-containing ores oxidized in a stream of $\text{O}_2 + \text{Al}_2\text{O}_3$ and $\text{KNO}_3$ .	Latschinow: <i>Russ. P.</i> <b>38</b> , 135, Aug. 31, 1934.
Synthesis of $\text{NH}_3$ . $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ .	Synthesis in the vicinity of the cathode in the Geissler tube; the anode is Pt, Fe, Cu, Ni, or amalgamated Cu and Al.	Jolibois and Olmer: <i>Compt. rend.</i> , <b>201</b> , 62-64 (1935).
Catalytic synthesis of $\text{NH}_3$ (review).		Komarow: <i>Priroda</i> , <b>24</b> (7), 14-19 (1935).
Synthesis of $\text{NH}_3$ ; the reaction is assumed to be of the second order; the form of the reaction taking place at active places is postulated to be as follows: $2\text{K}_x + \text{N}_2 + \text{H}_2 = 2\text{K}_x\text{NH}$ followed by a hydrogenation of the imide to $\text{NH}_3$ .	Iron-activated aluminum oxide or $\text{K}_2\text{O}$ ; the activation energy believed to represent the supply of energy which molecules of $\text{H}_2$ and $\text{N}_2$ must possess by colliding with an active particle is determined to be -21 k. cal.; Fe-K catalyst used by Maxted had an activation energy -18.6 k. cal.; $\text{FeCO}_3$ (natural siderite) used by Usatschew had an activation energy -22.6 k. cal.	Finkelstein and Rubanik: <i>Zhur. Fiz. Khim.</i> , <b>6</b> , 1051-1058 (1935).
Synthesis of $\text{NH}_3$ .	Fe oxide.	Kagan, Morozow and Podurovskaja: <i>Ibid.</i> , <b>8</b> , 677-688 (1936). Dubrowskaja and Kobosew: <i>Ibid.</i> , <b>8</b> , 234-243 (1936).

Table 4 (Continued).

Reaction	Catalyst	Observer
Synthesis of $\text{NH}_3$ (imide considered as an intermediate product).	Natural siderite, $\text{FeCO}_3$ ; activation energy with Fe-K (Maxted) = 18.6 k. cal.; with natural siderite (Ussatschew) = 22.6 k. cal.; with commercial Fe activated with $\text{Al}_2\text{O}_3$ or $\text{K}_2\text{O}$ (Finkelstein) = 21.0 k. cal.	Finkelstein and Rubanik: <i>Acta Physicochim. U.R.S.S.</i> , <b>3</b> , 945 (1936); <i>Zhur. Fiz. Khim.</i> , <b>6</b> , 1051-58 (1935); <b>8</b> , 793-94 (1936).
Synthesis of $\text{NH}_3$ ; yield of $\text{NH}_3$ , 13.5-17.0% at 200 atm. pressure.	Magnetic Fe ore is powdered, freed partially from $\text{SiO}_2$ and similar substances by a double treatment on a magnetic separator and melted after adding $\text{KNO}_3$ or $\text{Al}_2\text{O}_3$ ; the melt is powdered, cooled, treated again twice on the magnetic separator to bring $\text{SiO}_2$ content to 0.3-0.4%.	Kamsolkin, Koshenowa, Liwshitz and Schechin: <i>Russ. P.</i> 42,990, May 31, 1935.
Synthesis of $\text{NH}_3$ ; T. 425-500°; 250 atm.; space velocity, 15,000.	Crude and chromated siderite (roasting through melting); it is believed that the form in which Fe is present in the starting material (whether as $\text{Fe}_3\text{O}_4$ or siderite) is not essential for the activity of the catalyst.	Feldman, Iwanow and Naumowa: <i>Zhur. Khim. Prom.</i> , <b>12</b> , 1036-38 (1935).
Synthesis of $\text{NH}_3$ at high pressures and temperatures.	Ultrasonic waves instead of a catalyst.	Sseljakow and Bogdassorowa: <i>Russ. P.</i> 48,259, Aug. 31, 1936.
Synthesis of $\text{NH}_3$ .	Fe melted with activators $\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}$ subjected to the action of ultrasonic waves.	Sseljakow: <i>Russ. P.</i> 48,210, Aug. 31, 1936.
Synthesis of $\text{NH}_3$ .	Metallic rhenium.	Zenghelis and Stathis: <i>Praktika Akad. Athenon</i> , <b>11</b> , 487-90 (1936).
Synthesis of $\text{NH}_3$ .	Fe oxide; activity is increased more strongly by simultaneous presence of $\text{K}_2\text{O}$ and almost equal amount of $\text{Al}_2\text{O}_3$ (about 1%) than by $\text{Al}_2\text{O}_3$ alone; $\text{K}_2\text{O}$ covers more than one-half of the total surface of the catalyst (ascertained from adsorption isotherms for CO and $\text{N}_2$ at -183° and for $\text{CO}_2$ at -78.5°; at -183° CO forms a monomolecular chemically sorbed film on Fe atoms of the catalyst, while $\text{CO}_2$ at -78.5° is bound merely to the parts of the catalyst surface covered with the alkali.	Emmett and Brunauer: <i>J. Am. Chem. Soc.</i> , <b>59</b> , 310-15 (1937).
Synthesis of $\text{NH}_3$ ; initial temperature for gases, 190°; leave the contact at temperature 700°.	Chamotte, silicic acid, or Alundum impregnated with $\text{H}_2\text{PtCl}_6$ solution, heated to decompose the chloride.	N. V. de Bataafsche Petroleum Maatschappij: <i>E.P.</i> 464,706, May 20, 1937.
Synthesis of $\text{NH}_3$ ; T. 85°; nitrogen used <i>in statu nascendi</i> causes the yield to increase considerably.	Rhenium finely dispersed on pumice; addition of Fe increases the yield little.	Zenghelis and Stathis: <i>Oesterr. Chem.-Ztg.</i> , <b>40</b> , 80-81 (1937).
Synthesis of $\text{NH}_3$ .	Fe or Fe oxide containing difficultly reducible metal oxides and mixed with finely grained metals of the difficultly reducible oxides; mixing occurs by mechanical means; Ca, Mg, Al, which have a reducing action on the oxides may be added.	Harter: <i>G.P.</i> 647,720, Kl 12k, July 10, 1937.
Synthesis of ammonia.	Hämatite: $\text{Fe}_2\text{O}_3$ $\text{FeO}$ $\text{Al}_2\text{O}_3$ $\text{Mn}_2\text{O}_4$ $\text{SiO}_2$ $\text{CaO}$ $\text{MgO}$ Sulfide-S Sulfate $\text{Pd}_2\text{O}_3$	Grinewitsch and Klaptschuk: <i>Zhur. Priklad. Khim.</i> , <b>10</b> , 1868-1870 (1937). % 96.70 0.53 0.90 traces 1.6 0.09 0.05 0.004 0.02 0.04

Table 4 (Continued).

Reaction	Catalyst	Observer
Synthesis of ammonia.	Fe catalyst with 2.5-3.0% $K_2O$ and 7-8% $Al_2O_3$ is not so readily reduced as an Fe catalyst with 2% $K_2O$ and 4% $Al_2O_3$ ; catalysts of almost equal composition but melted under various conditions of temperature and pressure behave differently by reduction; a catalyst obtained from Fe—Mo by oxidizing and melting shows, after addition of $K_2O$ and $Al_2O_3$ , poor reduction and moderate activity but high stability; addition of $CuO$ or $NiO$ to an Fe catalyst activated with difficultly reducible oxides causes marked shortening of the reduction time but decreases the activity; reduction of the catalyst carried out so that an accumulation of water vapor in the gas phase on the catalyst takes place is disadvantageous, because it increases the reduction duration and the activity of the catalyst; the streaming velocity of the reducing gas mixture has to be such that the $H_2O$ vapor is removed to the extent to which it is formed; under the same conditions temperature increase from 375-500° causes shortening of the time necessary for complete reduction of the catalyst and an increase of activity; pressure increase from 1-300 atm. at small space velocity (1000) leads to a decrease of activity.	Latschinow: <i>Ibid.</i> , 10, 1847-1867 (1937).
Ammonia synthesis; T. -184 to +450°; for this temperature interval activated sorption of $H_2$ and $N_2$ is established; the velocity of the sorption process increases parallel to the increase of catalytic activity; the velocity of $NH_3$ formation at 375° corresponds approximately to the velocity of $N_2$ sorption under identical conditions; the activation energy of synthesis is considerably smaller than the activation energy of $N_2$ sorption; the mechanism of $NH_3$ synthesis is explained on the basis of the assumption that in the stage determining the velocity of the process simultaneously both $N_2$ and $H_2$ are taking part insofar as a specific sorption converts both into a reactionable state.	Fe—Mo— $Al_2O_3$ .	Gauchman and Roiter: <i>Zhur. Fiz. Khim.</i> , 11, 569-577 (1938).
Synthesis of ammonia; T. 400-525°; pressure, 200 and 300 atmospheres.	Granular magnetite with the addition of 4.5% $Al_2O_3$ and 5.3% $KNO_3$ (corresponding to 2.5% $K_2O$ ) is heated to melting with two water-cooled electrodes; one of these electrodes is connected with a third electrode by means of which heating is effected up to a temperature at which magnetite becomes conducting; the melted product, after reduction with a $N_2$ - $H_2$ mixture at 500°, is tested for its catalytic activity; the surface layer of the catalyst is considerably poorer in FeO than the internal mass, for it consists principally of $Fe_2O_3$ ; melts up to 50% $Al_2O_3$ may be prepared.	Telegin and Sidorow: <i>Zhur. Priklad. Khim.</i> , 11, 588-96 (1938); 11, 1064-70 (1938).

Table 4 (Continued).

Reaction	Catalyst	Observer
Synthesis of ammonia; the formation of $\text{NH}_3$ is considered as a desorption following the adsorption of poison on the catalyst (according to Morosow and Kagan, a washing out of $\text{NH}_3$ through $\text{H}_2$ and hydrogenation of adsorbed $\text{N}_2$ or nitride takes place); according to Jerofejef's experiments, a true hydrogenation should be hindered by $\text{K}_2\text{O}$ , while the desorption of $\text{NH}_3$ described by Morosow and Kagan is rather accelerated by $\text{K}_2\text{O}$ .	Iron.	Jerofejef: <i>Acta Physicochim. U.R.S.S.</i> 10, 313-15 (1939).

## PART III

## Catalytic Synthesis in Organic Chemistry

Table 1. Catalytic Synthesis of Methane (from Carbon Monoxide and Hydrogen Mixtures).

Reaction	Catalyst	Observer
Synthesis of $\text{CH}_4$ .	Ni or Co.	Mond and Langer: B.P. 12,608 (1888).
Synthesis of $\text{CH}_4$ $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ $2\text{CO} + 4\text{H}_2 \rightarrow 2\text{CH}_4 + \text{O}_2$ (at ordinary pressure; industrial process).	Ni.	Elworthy: E.P. 12,461 (1902). E.P. 14,333 (1904). G.P. 161,666 (1902). Sabatier: F.P. 354,621 (1905).
Synthesis of $\text{CH}_4$ $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ (at ordinary pressure).	Ni, Co, Fe.	Sabatier: F.P. 355,900 (1905). E.P. 15,326 (1906).
	Ni.	Vignon: F.P. 416,699 (1909). E.P. 186,900 (1923). G.P. 364,978 (1920).
	Ni.	
	Ni + $\text{Al}_2\text{O}_3$ .	Badische Anilin- und Soda Fabrik: G.P. 366,791 (1921). G.P. 396,115 (1923). Sabatier and Senderens: <i>Compt. rend.</i> , 134, 514 (1902). Medsforth: <i>J. Chem. Soc.</i> , 123, 1452 (1923). Neumann and Jacob: <i>Z. Elektrochem.</i> , 30, 557 (1924).
Synthesis of $\text{CH}_4$ .	Ni, Fe, or Mn.	Ellis and Elfred: U.S.P. 1,854,157 (1907).
Synthesis of $\text{CH}_4$ .	Ni, Co, Fe with activators.	Badische Anilin- und Soda Fabrik: B.P. 26,770 (1912). U.S.P. 1,113,096 (1912). U.S.P. 1,207,707 (1913).
Synthesis of $\text{CH}_4$ .	Fe, Co, or Ni, or their oxides.	Badische Anilin- und Soda Fabrik: G.P. 292,615 (1912).
Synthesis of $\text{CH}_4$ .	Ni.	Ipatieff: <i>J. prakt. Chem.</i> , 87, 479 (1912); <i>Zhur. Fiz. Khim.</i> 45, 433 (1913).
Synthesis of $\text{CH}_4$ .	Ni + 10% Th on pumice; Ni (NiO) on $\text{MgO}$ ; Ni + $\text{Al}_2\text{O}_3$ .	Badische Anilin- und Soda Fabrik: G.P. 306,301 (1914).
Synthesis of $\text{CH}_4$ .	Mo as well as W.	Deutsche Glühfadenfabrik: G.P. 362,462 (1921).
Synthesis of $\text{CO} + \text{H}_2$ to hydrocarbon (at ordinary pressure; industrial process) $\text{CO} + \text{water vapor}$ to liquid hydrocarbons.	Ni. Co—Fe— $\text{Cr}_2\text{O}_3$ in the presence of KOH. Fe + Cu; Co + ZnO; Ce + Cr; ZnO + $\text{Cr}_2\text{O}_3$ .	Scherb: Dissertation, Zürich (1923). Fischer and Tropesch: E.P. 255,818 (1926). F.P. 613,200 (1926). <i>Brennstoff-Chem.</i> , 7, 97 (1926). Patart: E.P. 247,178 (1925). F.P. 593,648 (1925). I. G. Farbenindustrie A.-G.: E.P. 312,717 (1927). F.P. 660,133 (1927).
	Fe(Co) + alkali, 0.4-0.6%.	

Table 1 (Continued).

Reaction	Catalyst	Observer
Synthesis of CO+H <sub>2</sub> to olefin-rich hydrocarbon (at ordinary pressure).	Co <sub>2</sub> O <sub>3</sub> , CuO, MnO <sub>2</sub> . Fe (containing small amounts of S); activated by alkali.	Nash, Bowen and Elvins: E.P. 291,867 (1927). I. G. Farbenindustrie A.-G.: E.P. 322,284 (1928). F.P. 677,973 (1928).
Synthesis of CH <sub>4</sub> .	Co <sub>2</sub> O <sub>3</sub> +Al <sub>2</sub> O <sub>3</sub> +K <sub>2</sub> O. Fe <sub>2</sub> O <sub>3</sub> +Al <sub>2</sub> O <sub>3</sub> +K <sub>2</sub> O.	Dupont (Lazier): B.P. 272,555 (1927).
Preparation of hydrocarbons: 21% CH <sub>4</sub> ; 45% lower hydrocarbons; 34% hydrocarbons suitable as motor fuel.	Co+Mn+Cu in a mixture.	Smith, Hawk and Reynolds: <i>Ind. Eng. Chem.</i> , <b>20</b> , 1341 (1929).
Synthesis of CH <sub>4</sub> .	Ni.	Perry and Fulweiler: B.P. 340,822, June 5, 1929.
Synthesis of CH <sub>4</sub> .	Ni.	Fischer and Tropsch: G.P. 484,337, Kl 12o, Gr 1, Oct. 16, 1929.
Synthesis of CH <sub>4</sub> (mixture formation of aliphatic and cyclic hydrocarbons to C <sub>4</sub> -C <sub>20</sub> ; T. 260-311° (industrial process)).	Fe oxide+Co oxide. Fe oxide+Ni oxide adding as promoters Cu and ZnO or Mn.	Berl and Jungling: <i>Z. angew. Chem.</i> , <b>43</b> , 435-440 (1930).
Synthesis of CH <sub>4</sub> .	ZnO-Cr <sub>2</sub> O <sub>3</sub> .	Garner and Kingman: <i>Nature</i> , <b>126</b> , 352 (1930).
Synthesis of CH <sub>4</sub> .	Ni.	I. G. Farbenindustrie A.-G.: F.P. 694,076, Nov. 28, 1930. G.P. 499,821, Kl 12o, Gr 1, July 4, 1930.
Synthesis of CH <sub>4</sub> . CO+3H <sub>2</sub> →CH <sub>4</sub> +H <sub>2</sub> O.	Ni (pure).	Bruckner and Jacobs: <i>Brennstoff-Chem.</i> , <b>14</b> , 265-268 (1933).
Synthesis of CH <sub>4</sub> .	Fe-Cu.	Odell: U.S.P. 1,984,380, Dec. 18, 1934.
Synthesis of CH <sub>4</sub> from CO and H <sub>2</sub> : T. 270°; up to 98.0% CO converted into CH <sub>4</sub> . T. 225°; up to 16.1% CO converted into CH <sub>4</sub> . T. 225°; CO <sub>2</sub> and CH <sub>4</sub> simultaneously formed. T. 350-400°; CO <sub>2</sub> and CH <sub>4</sub> simultaneously formed; higher temperature causes increase of CO <sub>2</sub> .	(1) Ni. (2) Ni-Mn. (3) Ni-Mn-Al <sub>2</sub> O <sub>3</sub> . (4) Mo.	Rapoport and Bljadow: <i>Khim. Tverdogo Topliva</i> , <b>5</b> , 625-632 (1934).
Synthesis of CH <sub>4</sub> from CO and H <sub>2</sub> ; T. 300-400°; 10-20 atm. pressure; yield 50% vol.	Ni mixed with Mn, Al. Ni-Mn-Al-Fe. Ni-Mn-Al-Mg on kieselguhr or active charcoal; Ni-Mn-Al (most active and readily regenerated).	Padovani and Franchetti: <i>Atti Congr. naz. chim. pura applicata II</i> , <b>5</b> , 818-828 (1936).
Synthesis of CH <sub>4</sub> from CO and H <sub>2</sub> .	Paraffins (forming a protecting envelope) + liquid substances introduced in a dispersed state.	Ruhr Chemie A.-G.: F.P. 802,536, Sept. 7, 1936.
Synthesis of CH <sub>4</sub> from CO and H <sub>2</sub> ; yield 50%; remainder consists of alcohols: methanol, ethanol and higher alcohols.	Co(NO <sub>3</sub> ) <sub>2</sub> +comm. KMnO <sub>4</sub> containing Zn(MnO <sub>4</sub> ) <sub>2</sub> .	Taylor: <i>Gas World</i> , <b>104</b> , No. 2696, April 4, 1936.
Synthesis of H <sub>2</sub> and CO to CH <sub>4</sub> .	High molecular weight products ppt. on contact, e.g., Fe with 5% Al <sub>2</sub> O <sub>3</sub> cause fatigue of the catalyst; it is suggested for preventing fatigue to spray into the gas mixture (entering from the top of the reaction tower) a solvent, e.g., paraffin oil, so that while the contact is continuously washed no liquid layer may accumulate in the reaction space.	I. G. Farbenindustrie A.-G.: E.P. 464,308, May 13, 1937. F.P. 814,853, July 1, 1937.



Table 1 (Continued).

Reaction	Catalyst	Observer
Synthesis of methane from CO and H <sub>2</sub> in the presence of water vapor:	(1) ThO <sub>2</sub> , CeO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> . (2) K <sub>2</sub> CO <sub>3</sub> (3) Ni containing 99% ThO <sub>2</sub> and 1% CeO <sub>2</sub> (uniform and active surface for the reaction); the slow loss of activity of sugar coal-Ni catalyst (these catalysts are prepared by impregnating pumice with a solution of cane sugar, nickel nitrate and other reagents and reducing at 300°) in the conversion of CO and H <sub>2</sub> is ascribed to carbon precipitation according to the equation: 2CO $\rightleftharpoons$ C + CO <sub>2</sub> (in the case of these catalysts the carbon precipitation must be inhibited to maintain their activity).	Chakravarty: <i>Z. anorg. allgem. Chem.</i> , <b>237</b> , 381-387 (1938).
(1) $C + H_2O \rightleftharpoons CO + H_2$ $C + 2H_2O \rightleftharpoons CO_2 + 2H_2$ (2) $2CO \rightleftharpoons C + CO_2$ (3) $CO + H_2O \rightleftharpoons CO_2 + H_2$ $2CO + 2H_2 \rightleftharpoons CH_4 + CO_2$ and possibly the catalyst (3) is also characteristic for the conversion: $CO + 3H_2 \rightarrow CH_4 + H_2O$ .		
Synthesis of hydrocarbons from CO and H <sub>2</sub> to large amounts of paraffins.	Paraffins are removed from the catalyst more frequently than required for regeneration of the catalyst, by extractions or treatment with H <sub>2</sub> at the temperature of synthesis; a mixture of benzene with higher boiling hydrocarbons is especially suitable as a solvent.	Ruhrenchemie A.-G.: F.P. 48,512, March 8, 1938; add to F.P. 812,883; (Refer to C. 1937 II 3953).
Synthesis of hydrocarbons or oxygen-containing derivatives from CO and H <sub>2</sub> .	A metal obtained by decomposition of the carbonyl compound (especially of Fe) which is pressed in the form of globules; (the catalyst is prepared according to the chief patent by thermal treatment of a metal of the Fe group at temperatures above 500° but below the melting point of the metal, and for such a long time that at least partial sintering of the metal takes place); it is advantageous to heat the metal in a reducing gas (H <sub>2</sub> ) or in vacuum to 600-1000°, likewise after superficial oxidation.	I. G. Farbenindustrie A.-G.: E.P. 490,090, Sept. 8, 1938; refer also to E.P. 473,932; (Refer to C. 1938 I 4766).
Synthesis of hydrocarbons from CO and H <sub>2</sub> ; conversion of gaseous hydrocarbons (especially methane, ethane, propane) with O <sub>2</sub> , CO <sub>2</sub> and water vapor at 820-1100°; thereby the exothermal reaction is bound with O <sub>2</sub> with endothermal reactions for CO <sub>2</sub> and H <sub>2</sub> O; previously the gas is desulfurized; synthesis takes place in the known manner; from reaction products are separated the gaseous and the too high boiling hydrocarbons and converted together at 540° under 70 atm. into liquid hydrocarbons.	Ni.	Kellogg Co.: F.P. 832,038, Sept. 20, 1938.
Synthesis of hydrocarbons from CO and H <sub>2</sub> ; initial ratio 1 : 2 to 1 : 1; process in one stage at about 200°; process in two stages at 187-216°; in the one-stage process liquid products originate with less olefins (28%) than in the two-stage (35%) or many-stage; the products, benzene, Diesel oil, are catalytically hydrogenated; lower hydrocarbons are dehydrogenated and then (e.g., with H <sub>3</sub> PO <sub>4</sub> ) polymerized; higher hydrocarbons are cracked and by halogenation and dehalogenation converted into lubricating oils; temperature increase in the catalyst by passage of gas is prevented if 6 l. gas are passed per hour, gradually in-	Ni or Co.  Ni.	Synthetic Oils, Ltd. (Myddleton): F.P. 830,560, Aug. 3, 1938. E.P. 491,778, Oct. 6, 1938. Robinson-Bindley Processes, Ltd. (Myddleton): E.P. 495,575, Dec. 15, 1938.

Table 1 (Continued).

Reaction	Catalyst	Observer
creasing the passage to 900 l. per hour; the catalyst is never heated more than 17° above desired temperature; the catalyst is placed into a tube 1 inch in diameter and 18 m. in length which is arranged between two concentric cylindrical surfaces washed with a cooling liquid.		
Synthesis of liquid hydrocarbons from CO and H <sub>2</sub> in streaming system; T. 190° and 200°; the brutto conversion velocity scarcely depends on the ratio amount of catalyst to carrier; the yield in liquid hydrocarbons increases with the kieselguhr content, the formation of gaseous hydrocarbons by too great hydrogenation activity of the catalyst, as well as CO <sub>2</sub> formation because of the increase in the amount of kieselguhr; by a ratio of Co : kieselguhr, 3 : 4, the yield of liquid hydrocarbons with respect to the amount of CO used is 85%.	Co (5%), Cu (12%), U <sub>3</sub> O <sub>8</sub> (the catalyst is obtained by precipitation of oxides of Co and Cu in the presence of kieselguhr and reduction of the oxides dried at 100° and mixed with ammonium uranate at the desired temperature).	Tsutsumi: <i>Sci. Papers Inst. Phys. Chem. Research (Tokyo)</i> , <b>35</b> , 435-40 (1939).
Synthesis of liquid hydrocarbons from CO and H <sub>2</sub> over Cu-free cobalt catalysts on kieselguhr as carrier; T. 210°; the activity of Co catalysts is increased considerably by precipitation in the presence of kieselguhr; reduction temp. 250°, 300°, 350°, 400°, and 450°; the decrease of activity by increase of the reduction temp., which is greatest in the case of Co-Mn and smallest in the case of Co-U <sub>3</sub> O <sub>8</sub> , may be greatly decreased by suitable additions of kieselguhr; the activity of Co-U <sub>3</sub> O <sub>8</sub> catalysts is greater than that of Co-ThO <sub>2</sub> catalysts and considerably greater than that of the Co-Mn catalysts.	ThO <sub>2</sub> (18% and 22%). U <sub>3</sub> O <sub>8</sub> (12%). Mn (15%, 20% and 24%) the increase in the promoter content acts qualitatively just like an increase in the carrier content because both make difficult the sintering of the reduced Co; the greater the activity of the promoter-containing catalysts, the smaller is the lowering of their activity by an increase in the reduction temperature.	Tsutsumi: <i>Ibid.</i> , <b>35</b> , 441-46 (1939).
Synthesis of hydrocarbons from CO and H <sub>2</sub> .		Ruhrchemie A.-G. (Alberts): F.P. 836,273, Jan. 13, 1939. E.P. 502,771, April 20, 1939. Austrian P. 106,931, April 20, 1939. Indian P. 25,177, April 1, 1939.
Synthesis of hydrocarbons and their oxygen derivatives from CO and H <sub>2</sub> ; T. 150-450°; 5-100 atm. pressure; gaseous, liquid, and solid hydrocarbons, alcohols, ketones, aldehydes, esters, and acids are obtained.	Catalyst prepared from metal compounds, especially of the 8th group, e.g., precipitated iron hydroxide with 3% Al(OH) <sub>3</sub> first reduced at a temp. below 500° (300-450°) without sintering in the presence of reducing gases (H <sub>2</sub> , CO, CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> ) and then subjected to a heat treatment at a temperature above 500° (especially 600-1000°) in the presence of non-oxidizing gases (N <sub>2</sub> , A, H <sub>2</sub> ), or in vacuum for such a long time that at least partial sintering of the reduced catalysts takes place, but no melting.	I. G. Farbenindustrie A.-G.: E.P. 496,880, Jan. 5, 1939.

Table 2. Catalytic Synthesis of Methanol (Industrial Process).

Reaction	Catalyst	Observer
Synthesis of methanol, higher alcohols, and saturated and unsaturated hydrocarbons from CO+H <sub>2</sub> and CO <sub>2</sub> +H <sub>2</sub> (under pressure).	With alkalis activated metals of the 8th group, oxides of Ce, Cr, Mn, Mo, Ti, Zn, or their mixtures.	Badische Anilin- und Soda Fabrik (Mittasch and Schneider): G.P. 293,787 (1913).
Carbides of Fe metals.		Badische Anilin- und Soda Fabrik: G.P. 295,203 (1914).

Table 2 (Continued).

Reaction	Catalyst	Observer
Synthesis of methanol from CO + H <sub>2</sub> and CO <sub>2</sub> + H <sub>2</sub> under pressure; hydrocarbon-free product-synthol (Fischer).	Ni, Ag, Cu, Fe. Fe + Cs (Rb).	Patart: F.P. 540,543 (1921). Fischer and Tropsch: G.P. 411,216 (1922).
Formation of methanol, higher alcohols, and "synthol"; higher alcohols are formed by reduction of aldehydes which result from reduction of acids, which in turn result from the addition of CO to the alcohol containing one less carbon atom; as mechanism for the formation of normal primary alcohols is proposed: C <sub>2</sub> H <sub>5</sub> OH = C <sub>2</sub> H <sub>5</sub> COOH C <sub>2</sub> H <sub>5</sub> COOH = C <sub>2</sub> H <sub>5</sub> CHO C <sub>2</sub> H <sub>5</sub> CHO = C <sub>2</sub> H <sub>5</sub> CH <sub>2</sub> OH		Fischer and Tropsch: <i>Brennstoff-Chem.</i> , 2, 246 (1924).
Synthesis of pure methanol from CO + H <sub>2</sub> and CO <sub>2</sub> + H <sub>2</sub> (under pressure).	Difficultly reducible metal oxides: CuO + Cr <sub>2</sub> O <sub>3</sub> (ZnO, MnO) 2-10 ZnO + 1 CrO <sub>3</sub> ZnO + CrO + Mn <sub>2</sub> O <sub>3</sub> ZnO + Cr <sub>2</sub> O <sub>3</sub> .	Badische Anilin- und Soda Fabrik (Mittasch, Pier and Winkler): F.P. 571,356 (1923). Badische Anilin- und Soda Fabrik: F.P. 580,905 (1923). G.P. 415,686 (1923). G.P. 441,433 (1923). Patart: F.P. 593,650 (1925).
Synthesis of methanol.	Cr <sub>2</sub> O <sub>3</sub> + ZnO ZnO + UO <sub>2</sub> ZnO + V <sub>2</sub> O <sub>5</sub> ZnO + WO <sub>3</sub> MgO + MoO <sub>3</sub> CeO <sub>2</sub> + Mn <sub>2</sub> O <sub>3</sub> CuO + ZnO	Badische Anilin- und Soda Fabrik: U.S.P. 1,558,559, Oct. 27, 1925. Can. P. 251,483, July 7, 1925. Can. P. 251,484, July 7, 1925. E.P. 229,714, March 26, 1925. F.P. 571,354, May 16, 1924. F.P. 605,349, 1926. E.P. 266,405, Feb. 21, 1927.
Synthesis of methanol.	Zn and Cr oxides called best catalyst, persistent in activity, not sensitive to poisons and readily regenerated.	Patart: <i>Proc. Intern. Conf. Bituminous Coal</i> , 141 (1926).
Synthesis of methanol.	Cu, Cu(OH) <sub>2</sub> .	Société Nationale de Recherche pour le Traitement des Combustibles: F.P. 613,896, Dec. 1, 1926.
Synthesis of methanol.	Sr or Zn; PbO or Bi <sub>2</sub> O <sub>3</sub> .	Société Française de Catalyse Généralisée: E.P. 265,948, April 6, 1927.
Synthesis of methanol.	Zn carbonate precipitated from a very dilute solution in the presence of protective colloids: starch, saponin, pectin, or hydrated silica; electrolytes removed by washing and the Zn carbonate gel dried by heating under reduced pressure; converted into the oxide at 250-400°C.	British Celanese, Ltd.: B.P. 300,142, May 2, 1927.
Synthesis of methanol; T. 350-400°C. T. 420°C. 200 atm.; space velocity, 33,300; yield 95% methanol, 1% higher alcohols and 4% H <sub>2</sub> O.	Cr-Zn catalyst (prepared from basic or normal Zn chromate). 3ZnO-CrO <sub>3</sub> .	Morgan, Taylor and Hedley: <i>J. Soc. Chem. Ind.</i> , 47, 117T (1928).
Synthesis of methanol; yield, 26%. yield, 9%.	3 mol % ZnO + 97 mol % CuO (prepared from hydroxides of Zn and Cu). Pure CuO.	Frolich, Fenske and Quiggle: <i>Ind. Eng. Chem.</i> , 20, 694 (1928).
Synthesis of methanol.	44% CuO + 36% ZnO + 20% alumina.	Lewis and Frolich: <i>Ind. Eng. Chem.</i> , 20, 287 (1928).

Table 2 (Continued).

Reaction	Catalyst	Observer
Synthesis of methanol under 150 atm. $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$ yield, 17.5%; side reactions are: $2\text{CO} = \text{C} + \text{CO}_2$ $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$ $2\text{CO} + 2\text{H}_2 = \text{CH}_4 + \text{CO}_2$ $\text{MnO}_2$ , yield 5%. $\text{ZrO}_2$ $\text{CeO}_2$ $\text{UO}_2$ } yield 2%.	ZnO (metallic Fe, Ni or Co are not suitable for methanol synthesis because, although they are often active in reducing CO to methanol, they have a more pronounced effect on side reactions leading to production of C, $\text{CO}_2$ and $\text{H}_2\text{O}$ ).	Audibert and Raineau: <i>Ind. Eng. Chem.</i> , 20, 1105 (1928).
Synthesis of methanol.	Zn (prepared by precipitating hot solutions of $\text{Zn}(\text{NO}_3)_2$ with $\text{Na}_2\text{CO}_3$ and washing it free from the nitrate; the moist precipitate is pressed into threads).	Brown and Galloway: <i>Ind. Eng. Chem.</i> , 20, 960 (1928).
Synthesis of methanol; T. 500–600°.	$\text{Ni}(\text{OH})_2$ , NiO, $\text{Ni}(\text{NO}_3)_2$ , Ni oxalate.	Compagnie de Béthune: F.P. 633,139, Jan. 21, 1928.
Synthesis of methanol.	Ni formate + Cr formate.	Compagnie de Béthune: F.P. 632,259, Jan. 6, 1928.
Synthesis of methanol.	70–80 atoms Zn plus 20–30 atoms Cr.	Synthetic Ammonia and Nitrates, Ltd. (Franklin): E.P. 290,399, June 14, 1928. E.P. 293,056, July 26, 1928.
Synthesis of methanol.	Fe + Rb (Cs).	
Synthesis of methanol.	$\text{ZnCO}_3$ or $\text{ZnHCO}_3 + \text{H}_2\text{CrO}_4$ .	Imperial Chemical Industries, Ltd.: F.P. 642,318, Aug. 27, 1928.
Synthesis of methanol.	50% reduced Cu + 50% CeP.	Roessler and Hasslacher, Inc.: U.S.P. 1,707,331, April 2, 1929.
Synthesis of methanol.	Basic and acid oxides containing small amounts of alkali compounds: sulfates, phosphates, chromates, hydroxides, carbonates, or salts of organic acids.	Dupont (Lazier and Zeisberg): E.P. 313,093, July 31, 1929.
Synthesis of methanol.	Zn-Cr.	Nawitt, Byrne and Strong: <i>Proc. Roy. Soc. London (A)</i> , 123, 236–52 (1929).
Synthesis of methanol.	Zn chromate.	Brown and Galloway: <i>Ind. Eng. Chem.</i> , 21, 310–313 (1929).
Synthesis of methanol.	Cu (prepared from precipitated hydroxide).	Waterman and van Tussenbrock: <i>Chem. Weekblad</i> , 26, 410–413 (1929).
Synthesis of methanol T. 350°C.; 204 atm. 18% CO converted.	77 mol % Zn. 23 mol % Cr. Catalysts rich in Cr give large yields of $\text{CO}_2$ and unsaturated hydrocarbons, while those rich in Zn tend to produce methyl formate.	Frolich: <i>J. Soc. Chem. Ind.</i> , 47, 176T (1928). Cryder and Frolich: <i>Ind. Eng. Chem.</i> , 21, 867 (1929).
Synthesis of methanol.	$3\text{ZnO} \cdot 1\text{Cr}_2\text{O}_3$ + fractional percentage of Cu nitrate.	Bone: <i>Trans. Inst. Chem. Engrs. (London)</i> , 8, 102 (1930).
Synthesis of methanol; from 15.3% CO, 2.8% $\text{CH}_4$ , 30.6% $\text{H}_2$ , 51.3% $\text{N}_2$ .	Fe oxide.	I. G. Farbenindustrie A.-G. (Pier and Wietzel): U.S.P. 1,788,170, Jan. 5, 1931.
Synthesis of methanol $2n\text{ZnH}_2 + \text{Cu}(\text{CO})_n = \text{Cu} + 2n\text{Zn} + n\text{CH}_4\text{O}$ .	Zn-Cu.	Plotnikow and Kudra: <i>Zhur. Obschei Khim.</i> , 1 (63), 1075–1079 (1931).
Synthesis of methanol.	ZnO or $\text{Zn}(\text{OH})_2$ (prepared by electrolysis; pure with respect to alkalis).	British Celanese, Ltd. (Bader and Thomas): E.P. 345,649, April 23, 1931.
Synthesis of methanol.	ZnO-CuO.	Nussbaum and Frohlich: <i>Ind. Eng. Chem.</i> , 23, 1386 (1931).
Synthesis of methanol (gas mixture for synthesis: 35% CO and 49% $\text{H}_2$ ).	$\text{ZnNO}_3 + \text{MnNO}_3$ ; 190 g. and 18 g. each respectively replaced by a solution of 167 g. $\text{NH}_4$ chromate and 45 cc. $\text{NH}_4\text{OH}$ .	Dupont (Lazier): U.S.P. 1,829,046, Oct. 27, 1931.

Table 2 (Continued).

Reaction	Catalyst	Observer
Synthesis of methanol.	Reduction and oxidation catalysts used together (Fe, Ni, Co, Pd).	Selden Co. (Jaeger): U.S.P. 1,824,896, Sept. 29, 1931. Selden Co. (Jaeger and Bertsch): U.S.P. 1,840,450, Jan. 12, 1932.
Synthesis of methanol.	Zn + Cr <sub>2</sub> O <sub>3</sub> (prepared from carbonates).	Imperial Chemical Industries, Ltd.: U.S.P. 1,878,390, Sept. 20, 1932.
Synthesis of methanol; T. 150–450°, 5–300 atm. pressure.	Reduced Cu + CaO (Cu content does not exceed 50%) prepared from 236 p. Ca(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O and 100 p. Cu (NO <sub>3</sub> ) <sub>2</sub> · 3H <sub>2</sub> O.	Roessler and Hasslacher, Inc. (Storch): U.S.P. 1,875,273, Aug. 30, 1932.
Synthesis of methanol.	ZnO + Cr <sub>2</sub> O <sub>3</sub> + Li.	Kanzner: Swiss P. 150,613, Jan. 16, 1932.
Synthesis of methanol.	Zn(OH) <sub>2</sub> .	Dreyfus: F.P. 713,701, Oct. 31, 1932.
Synthesis of methanol; T. 250–300°, 100–200 atm. pressure.	Cu-Zn alloy, 1–2 p. Zn to 7.9 p. Cu or bronze with 3% Mn; also in the form of filings in which Cu content prevails.	Commercial Solvents Corporation (Gabriel and Brown): U.S.P. 1,875,722, Sept. 6, 1932.
Synthesis of methanol.	Zn-Cu-Al (Cu carbonyl supposed to be formed).	Boomer and Morris: <i>J. Am. Chem. Soc.</i> , <b>54</b> , 3080–3095 (1932).
Synthesis of methanol.	Zeolite. Silica gel or active charcoal.	Selden Co. (Jaeger and Bertsch): U.S.P. 1,840,450, Jan. 12, 1932. Kozan: Japan P. 96,341, June 21, 1932.
Synthesis of methanol.	Zn + Cr <sub>2</sub> O <sub>3</sub> .	Imperial Chemical Industries, Ltd.: U.S.P. 1,878,390, Sept. 20, 1932.
Synthesis of methanol.	Zn and Cr <sub>2</sub> O <sub>3</sub> in various proportions: ZnO + Al <sub>2</sub> O <sub>3</sub> ZnO + MgO ZnO + MnO ZnO + Cr <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub>	Strada: <i>Giorn. chim. ind. applicata</i> , <b>15</b> , 168–176 (1933).
Synthesis of methanol by saponification of halide alkyls in the vapor phase, e.g., chloromethyl dichloro-methane and benzo-trichloride: (1) CH <sub>2</sub> Cl + H <sub>2</sub> O → HCl + CH <sub>3</sub> OH (2) CH <sub>3</sub> OH → H <sub>2</sub> + CH <sub>2</sub> O (3) CH <sub>2</sub> O → H <sub>2</sub> + CO (4) CO + H <sub>2</sub> O → H <sub>2</sub> + CO <sub>2</sub>	Sn phosphate (20 g. SnCl <sub>4</sub> and 11.7 g. (90%) H <sub>3</sub> PO <sub>4</sub> on one mm. large grained pumice dried and treated with H <sub>2</sub> O vapor; T. 500–525°.	Abkin and Medwedew: <i>Zhur. Khim. Prom.</i> , <b>11</b> , 30–34 (1934).
Synthesis of methanol from CO and H <sub>2</sub> ; T. 400°, 200 atm. pressure; circulation velocity 200,000 reduced vol./hr. and vol. unit of the catalyst.	CuO + MnO; one g. equivalent of these compounds and addition of 0.05 g. equivalent of CoO; the Co phosphate, borate, sulfide or selenide may be used as additions; the Co sulfide gave the highest conversion of CO to C <sub>2</sub> H <sub>5</sub> OH; Fe, Mo sulfides are less active; Ni, inactive.	Taylor: <i>J. Chem. Soc.</i> , <b>1934</b> , 1429–31.
Synthesis of methanol.	Cu + Cr <sub>2</sub> O <sub>3</sub> ; the reaction takes place at the boundary Cu/CuO Cu + CuO + Cr <sub>2</sub> O <sub>3</sub> + ZnO (ZnO increases dispersion degree and stabilizes).	Iwanow: <i>Acta Physicochim. U.R.S.S.</i> , <b>1</b> , 493–502 (1934). Plotnikow and Iwanow: <i>Zhur. Obshchei Khim.</i> , <b>63</b> , 826–844 (1931).
Synthesis of methanol; the rate of the reaction is supposed to be controlled by the velocity of activated adsorption of the reacting gases.	Surfaces of ZnO and Mo <sub>2</sub> O <sub>3</sub> are much inferior to ZnO; Zn-Cr oxide surfaces enormously accelerate the reaction in comparison to ZnO surfaces.	Taylor and Strother: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 586 (1934).
Synthesis of methanol.	Pure ZnS.	Dolgow, Karpinski and Ssilina: <i>Khim. Tverdogo Topliva</i> , <b>3</b> , 470–74 (1935).
Synthesis of methanol at wide range of temperature and under 180 atm.	25 atomic % Cr and 75 atomic % Zn; both metals initially in the form of oxides (most active).	Molstad and Dodge: <i>Ind. Eng. Chem.</i> , <b>27</b> , 134 (1935).

Table 2 (Continued).

Reaction	Catalyst	Observer
Synthesis of methanol; T. 300-425°, 178 atm. gas passage, 25,000 l./l. contact/hr.; CO : H <sub>2</sub> = 1 : 2; yield, 96.0-99.8% CH <sub>3</sub> OH.	ZnO + Cr <sub>2</sub> O <sub>3</sub> ; Zn : Cr = 1 : 1; Cr not less than 25%, 8% Zn; the catalyst loses the catalytic property through rapid gas circulation; the catalyst is precipitated from Na <sub>2</sub> CO <sub>3</sub> or from 3-valent compound better than from a 6-valent compound.	Molstad and Dodge: <i>Ind. Eng. Chem.</i> , <b>27</b> , 134-40 (1935). Storch: <i>J. Phys. Chem.</i> , <b>32</b> , 1743-1744 (1928).
Synthesis of methanol.	Zn : Cu and Cr; 60 : 30 : 10 or 45 : 10 : 45, 2 4-1/2 atoms of Zn to one atom Cu.	Karpen and Bros. (Dodge): U.S.P. 2,014,883, Sept. 17, 1935.
High pressure synthesis of methanol; T. 400°, 200 atm.	Cr and Mn nitrate glowed.	Taylor: <i>Gas World</i> , <b>104</b> , No. 2696, April 4, 1936.
Synthesis of methanol; yield: 17% methanol, 22% ethanol and 11% higher alcohols.	One mol CuO, one mol MnO and 0.1 Mol CoS.	
Synthesis of methanol from CO + H <sub>2</sub> O; high temp. and high pressure.	ZnO, CrO <sub>3</sub> and CuO may contain ferro chromium the content of ZnO larger than that necessary for the formation of a chromate; the inside walls of the vessel of steel containing Cr and Ni.	Carbide and Carbon Chemicals Corporation (Eversole): Can. P. 359,414, July 28, 1936.
Synthesis of alcohols by hydrogenating a monosaccharide; T. 100-200°, diminished pressure; CaCO <sub>3</sub> should be present; second time hydrogenation new catalyst; T. 200-300°.	Ni.	Canadian Industries, Ltd. (Kothrock): Can. P. 362,016, Nov. 24, 1936.
Synthesis of monovalent alcohols; pressure below atm. pressure; from olefins and H <sub>2</sub> O and hydrolysis of H <sub>2</sub> SO <sub>4</sub> ester.	3.5 : 1 ethyl alcohol; H <sub>2</sub> SO <sub>4</sub> ; H <sub>2</sub> SO <sub>4</sub> : H <sub>2</sub> O ratio depends on the kind of alcohol: 2 : 3 tertiary amyl alcohol, 1 : 1 tertiary butyl alcohol, 3 : 2 isopropyl alcohol.	Standard Oil Co. of California: F.P. 799,076, June 5, 1936.
Synthesis of methanol.	Dried CuO and ZnO mixed with Cr <sub>2</sub> O <sub>3</sub> solution; CuO : ZnO : Cr <sub>2</sub> O <sub>3</sub> = 9 : 15 : 7.	Karpow: Russ. P. 47,687, July 31, 1936.
Synthesis of methanol from CO.	(Equipment chiefly described.)	Feldman and Chaikowa: <i>Zhur. Khim. Prom.</i> <b>13</b> , 970-75 (1936).
Synthesis of methanol from CO and H <sub>2</sub> ; short heating of the catalyst; T. 1050-1150° with joint reduction of CuO to Cu (catalyst so obtained stable against mechanical influences).	Mixture of CuO and Cu <sub>2</sub> O, 10-50%.	Ammonia Casale: F.P. 797,934, May 6, 1936.
Preparation of methyl alcohol and higher alcohols from gases containing C oxides and H <sub>2</sub> .	An alloy of the type: Cu-Al, Ag-Al, Cu-Si, Ag-Si treated with NaOH and furthermore with substances favorable for the formation of alcohol such as ZnO, CrO <sub>3</sub> .	"Montecatini" Società Generale per l'Industria Mineraria ed Agricola: Ital. P. 352,746, June 10, 1937.
Synthesis of primary and secondary alcohols.	Ni on kieselguhr, Ca chromite, Ca-Ba chromite.	
Synthesis of methanol.	Cu chromite, Cu carbonyl.	
Synthesis of methanol.	Oxides of Ce, Cr, Mn, Mo, Ti, Zn in a mixture: CuO + Cr <sub>2</sub> O <sub>3</sub> (ZnO or MnO) ZnO + Cr <sub>2</sub> O <sub>3</sub> Cr <sub>2</sub> O <sub>3</sub> + Zn + Mn <sub>2</sub> O <sub>3</sub> Fe activated by 0.4-0.6 alkali + small amount of sulfur.	
Synthesis of methanol.	Moor W; Fe carbide, Ce, Cr, Mn, Mo, Ti, Zn; Ni, Ag, Cu, Fe; activated Cu.	
Catalytic synthesis of methanol and side products.		Nikitin: <i>Prom. Org. Khim.</i> , <b>3</b> , 364 (1937).

Table 3. Catalytic Synthesis of Ethyl Alcohol.

Reaction	Catalyst	Observer
Synthesis of ethyl alcohol.	Oxides of V, U, Al, Cu, Ag, Pb, Zn in combination with metallic salts, activators or with metal oxides.	
Synthesis of ethyl alcohol; T. 140–180°.	Cu+Ni+MnO.	Anilin Fabrik A.-G.: G.P. 298,541, Aug. 2, 1916. G.P. 298,553, Aug. 1, 1916. Swiss P. 87,962, Jan. 17, 1921.
Synthesis of ethyl alcohol.	Alloys Cr-Mn and Cu-Zn.	Badische Anilin- und Soda Fabrik (Mittasch and Pier): U.S.P. 1,369,775, Jan. 12, 1926. E.P. 240,955, Nov. 5, 1925.
Synthesis of ethyl alcohol; T. 125–130°; 29–900 atm. pressure.	Volatile halides, such as HCl, HI, HBr, or CH <sub>3</sub> Cl, CCl <sub>4</sub> , C <sub>2</sub> H <sub>5</sub> Cl on pumice, silica gel, or coke.	Dorrell: <i>J. Chem. Soc.</i> , 127, 2399–2407 (1925). I. G. Farbenindustrie A.-G.: G.P. 568,546, Kl 120, Jan. 21, 1933.
Synthesis of ethyl alcohol.	MnO+2H <sub>3</sub> PO <sub>4</sub> MnO+2·5H <sub>3</sub> PO <sub>4</sub> MnO+2·7H <sub>3</sub> PO <sub>4</sub> MnO+3H <sub>3</sub> PO <sub>4</sub>	Distillers Co., Ltd.: E.P. 392,289, June 8, 1933. E.P. 392,685, June 15, 1933.
Synthesis of ethyl alcohol; T. 200°.	FeO+2H <sub>3</sub> PO <sub>4</sub> 2FeO+5H <sub>3</sub> PO <sub>4</sub> 2FeO+7H <sub>3</sub> PO <sub>4</sub> FeO+3H <sub>3</sub> PO <sub>4</sub>	Distillers Co., Ltd. (Stanley): E.P. 392,289, June 8, 1933.
Synthesis of ethyl alcohol; T. 200°; 250 atm. pressure.	1.0 mol boric acid anhydride + 2.2 mols H <sub>3</sub> PO <sub>4</sub> (in amount to form orthophosphates corresponding to 70% and not more than 95%); (100 cc. catalyst for 312 l. C <sub>2</sub> H <sub>4</sub> and 1.5 vol. water vapor).	Distillers Co., Ltd.: E.P. 396,724, Sept. 7, 1933.
Synthesis of ethyl alcohol.	U, Fe, or Co (or their compounds decomposable by H <sub>3</sub> PO <sub>4</sub> in amount larger than that corresponding to the orthophosphates but not more than 95%); FeO·2H <sub>3</sub> PO <sub>4</sub> or FeO·3H <sub>3</sub> PO <sub>4</sub> (prepared from ferrous oxalate and H <sub>3</sub> PO <sub>4</sub> ); 2CoO·5H <sub>3</sub> PO <sub>4</sub> +uranyl phosphate containing 25 mols of H <sub>3</sub> PO <sub>4</sub> per atom of U.	Distillers Co., Ltd.: B.P. 392,289, May 18, 1933. B.P. 392,685, May 25, 1933. E.P. 396,724, Sept. 7, 1933.
Synthesis of ethyl alcohol.	Cd metaphosphate.	Imperial Chemical Industries, Ltd. (Horsley): U.S.P. 1,893,586, Jan. 10, 1933.
Synthesis of ethyl alcohol.	CuO+MnO [1 g. equivalent of these compounds+0.05 g. equivalent CoO+0.1 g. equivalent Co phosphate, borate, sulfide, or selenide (sulfides of Fe, Mo less active; Ni sulfide inactive)].	Taylor: <i>J. Chem. Soc.</i> , 1934, 1429–1431. Morgan and Taylor: <i>Proc. Roy. Soc. London (A)</i> , 131, 533–540 (1931).
Synthesis of ethyl alcohol from water gas; T. 380–435°; 175–200 atm. pressure; 12% of CO converted into ethyl alcohol; 47% hydrogenated into CH <sub>4</sub> ; T. 400°; 200 atm. pressure; 17% methanol; 22% ethanol; 11% higher alcohols; 47% methane.	0.05 mols Co oxide+1.0 mol CuO+1.0 mol MnO.  10 : 10 : 1 molecular mixture – CuO : MnO : CoS <sub>2</sub> .	Taylor: <i>J. Chem. Soc.</i> , 1934, 1429–1431.
Synthesis of ethyl alcohol; T. 320–30°; 120 atm. pressure; yield, 39%+higher alcohols.	ZnO-CoO – 3 : 1 mol ratio	Klukwin, Volnov and Karpinskii: <i>Nefyanoe Khos.</i> , 2, 265 (1934).
Synthesis of ethyl alcohol from C <sub>2</sub> H <sub>4</sub> and water vapor; T. greater than 170°; pressure greater than 100 lbs./sq.in.; T. 250°; pressure 600 lbs.; ratio C <sub>2</sub> H <sub>4</sub> : H <sub>2</sub> O = 1 : 2; for 90 cu. ft./hr./l. catalyst, 10% conversion; T. 255–260°; pressure 1,000 lbs./sq.in.; ratio C <sub>2</sub> H <sub>4</sub> : H <sub>2</sub> O = 1 : 1.	H <sub>2</sub> SO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub> (relatively dilute); accelerators added to the acid: Ag <sub>2</sub> SO <sub>4</sub> or Li <sub>2</sub> SO <sub>4</sub> .  Conc. of H <sub>2</sub> SO <sub>4</sub> is 41%.  Conc. of H <sub>2</sub> SO <sub>4</sub> is 30%.	Air Reduction Co., Inc. (Metzger): U.S.P. 2,050,442 and U.S.P. 2,050,443, Aug. 11, 1936.

Table 4. Catalytic Synthesis of Butanol.

Reaction	Catalyst	Observer
Synthesis of butanol from ethanol. $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ T. 300–450°.	Fe, Fe + Ni, Fe <sub>2</sub> O <sub>3</sub> . Fe <sub>2</sub> O <sub>3</sub> + Ag <sub>2</sub> O + NiO. Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> + NiO (molecular amounts) upon bone charcoal as a carrier. Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> activated by Yt, Zr and La on bone charcoal.	Dolgow and Wolnow: <i>Zhur. Obshchei Khim.</i> , 3 (65) 313–318 (1933).
T. 400°; after 2 days yield 20–22% butanol + acetone ethylene polymers, acetaldehyde and traces of formaldehyde and di-amyl ether; CH <sub>3</sub> OH gave with the same catalyst considerable amounts of synthol-like products, while <i>n</i> -propyl, <i>n</i> -butyl and iso-amyl alcohols gave only simple ethers.		

Table 5. Catalytic Synthesis of Isopropyl Alcohol.

Reaction	Catalyst	Observer
Synthesis of isopropyl alcohol from acetone; T. 150–200°.	Cu + Ni + MnO.	Anilin Fabrik A.-G.: G.P. 298,541 (1917). G.P. 298,553. Swiss P. 87,962, Jan. 17, 1921
Synthesis of isopropyl alcohol.	Ni or Co.	Riedel A.-G.: G.P. 424,067, Kl 12g, Jan. 20, 1926.
Synthesis of isopropyl alcohol from acetone.	ZnO or other difficultly reducible oxides + basic compounds of an alkali such as K <sub>2</sub> CO <sub>3</sub> (depresses normal dehydrating action of the catalyst).	Lazier: U.S.P. 1,895,515, Jan. 31, 1933.

Table 6. Catalytic Synthesis of Higher Alcohols.

Reaction	Catalyst	Observer
Synthesis of higher alcohols (allyl alcohol).	Metals.	Brochet: <i>Compt. rend.</i> , 158, 1351–1353 (1913); <i>Bull. soc. chim.</i> , 15, 554–604 (1913).
Synthesis of higher alcohols (synthol).	Rb hydroxide most efficient alkali used for impregnating Fe chips.	Fischer and Tropsch: <i>Brennstoff-Chem.</i> , 5, 201, 217 (1924).
Synthesis of higher alcohols.	Pd on charcoal.	Commercial Solvents Corporation: G.P. 417,926, Kl 12o, Aug. 22, 1925.
Synthesis of higher alcohols from water gas; T. 400°; yield methanol, 82%; higher alcohols, 9%; water, 8%.	Basic Zn chromate + 10% Co chromate (Co chromate has a special property of linking C atoms).	Morgan, Taylor and Hedley: <i>J. Soc. Chem. Ind.</i> , 47, 117T (1928).
Synthesis of higher alcohols.	Uranium oxide.	Maihle and Renandie: <i>Compt. rend.</i> (1928).
Preparation of higher aliphatic alcohols and ethers separated from water and lower alcohols from water gas; T. 300–350°; 100 atm. pressure.	12 parts Fe, 2 parts Cd and 3 parts Cu (the metals are taken as nitrates, the mixture glowed and reduced).	I. G. Farbenindustrie A.-G.: E.P. 300,294 (1928).
Synthesis of higher alcohols (allyl alcohol).	Al <sub>2</sub> O <sub>3</sub> , ZnO.	Weston and Adkins: <i>J. Am. Chem. Soc.</i> , 51, 2430–2436 (1929).
Synthesis of higher alcohols from CO and H <sub>2</sub> ; high temp. and 200 atm. pressure.	ZnO + Cr <sub>2</sub> O <sub>3</sub> . ZnO + Mn <sub>2</sub> O <sub>3</sub> + Cu (catalyst contains CO).	Morgan and Taylor: E.P. 313,061, July 4, 1929.
Synthesis of higher alcohols.	Ni, Co, Cu or their oxides + Cr <sub>2</sub> O <sub>3</sub> (OH <sup>+</sup> contributed by organic or inorganic substances: CO <sub>2</sub> , SO <sub>4</sub> , borates, oxides, NH <sub>3</sub> , organic cmpds).	I. G. Farbenindustrie A.-G.: F.P. 694,424, Dec. 3, 1930.
Synthesis of higher alcohols.	Metal oxides (prepared from corresponding carbonates; used in the form of balls or tablets); ZnCO <sub>3</sub> (prepared from ZnSO <sub>4</sub> + Na <sub>2</sub> CO <sub>3</sub> ).	Jablezynski and Frenkenberg: <i>Bull. soc. chim.</i> , 4 (45) 210–217 (1930).
Artificial ageing of wines.	Metallic oxides: Pb > Cu > Ni > Mo > Co > Ti > Si.	Sandor: <i>Mesogazdasagi Kutatasok</i> , 4, 468–481 (1931).



Table 6 (Continued).

Reaction	Catalyst	Observer
Synthesis of higher alcohols; ratio olefin to water vapor = 1 : 2; T. 280°; 42 atm. pressure.	Strong acids of moderate conc., such as $\text{H}_2\text{SO}_4$ (41%) + $\text{H}_3\text{PO}_4$ containing $\text{AgSO}_4$ or $\text{LiSO}_4$ (favoring olefin adsorption).	Air Reduction Co., Inc.: P.P. 738,939, Dec. 31, 1932.
Synthesis of higher alcohols from 4 vol. olefins, 1-3 vol. $\text{O}_2$ ; 1 vol. olefin per 1-5 vol. $\text{H}_2\text{O}$ .	$\text{Cu}$ , $\text{CuO}$ , $\text{V}_2\text{O}_5$ , Mn compounds, Fe salts, $\text{I}_2$ perborates, persulfates, perchromates, W.	Dreyfus: P.P. 737,612, Dec. 14, 1932. P.P. 713,701, Oct. 31, 1932.
Synthesis of higher alcohols.	89 parts $\text{MgO}$ + 8 parts $\text{Al}_2\text{O}_3$ + 3 parts $\text{CuO}$ .	I. G. Farbenindustrie, A.-G.: E.P. 381,185, Oct. 27, 1932.
Synthesis of higher alcohols.	$\text{ZnO} + \text{CH}_3\text{COOK}$ (increase in the alkali content shifts to formation of higher alcohols instead of methanol).	Natta and Rigamonti: <i>Giorn. chim. ind. applicata</i> , <b>14</b> , 217 (1932).
Synthesis of higher alcohols (propyl alcohol); T. 150°.	Alumina + catalyst containing reduced Ni.	Young and Law: Can. P. 328,049, Nov. 29, 1932.
Synthesis of higher alcohols.	Formates and acetates have highest catalytic power; catalytic action due to the percentage of $\text{K}_2\text{O}$ rather than to its form, e.g., K salts of aliphatic fatty acids $\text{H} \cdot \text{COOK}$ , $\text{AcOK}$ , $\text{Et} \cdot \text{COOK}$ , $\text{Pr} \cdot \text{COOK}$ and $\text{Bu} \cdot \text{COOK}$ .	Strada: <i>Giorn. chim. ind. applicata</i> , <b>14</b> , 601-607 (1932).
Synthesis of higher alcohols; T. about 400° C.; yield 9.8% higher alcohols; methanol, 49.7%.	Basic catalyst containing a mixture of Cr and Mn oxides in molecular proportion impregnated with Rb hydroxide (Li, Na, K, Cs hydroxides were used with less success).	Morgan, Hardy and Proctor: <i>J. Soc. Chem. Ind.</i> , <b>51</b> , 1T (1932).
Synthesis of dodecyl and octadecyl alcohol; T. 250°; 178 atm. pressure.	$\text{Cu}$ chromate.	Henkel and Co.: P.P. 743,358, March 30, 1933.
Synthesis of higher alcohols; T. 125-130° 25-900 atm. pressure.	Volatile halides: $\text{HCl}$ , $\text{HI}$ , $\text{HBr}$ or $\text{CH}_3\text{Cl}$ , $\text{C}_2\text{H}_5\text{Cl}$ , $\text{CCl}_4$ , $\text{NH}_4\text{Cl}$ on pumice, silica gel or coke.	Dupont: U.S.P. 2,014,740, Sept. 17, 1935.
Synthesis of alcohol from ether and water; T. 200-300°; pressure greater than 225 lbs./sq. in.; e.g., T. 272° 2,000 lbs./sq.in.	10% $\text{H}_2\text{SO}_4$ , $\text{H}_3\text{PO}_4$ , $\text{HCl}$ organic acids, such as acetic acid, aqueous solutions of $\text{AlCl}_3$ , $\text{ZnCl}_2$ , Ag salts, mineral oils, fatty oils, Turkey-red oil, etc., may be added to raise activity.	Standard Oil Development Co. (Lewis): U.S.P. 2,045,785, June 30, 1936.

Table 7. Catalytic Synthesis of Formaldehyde.

Reaction	Catalyst	Observer
Synthesis of formaldehyde.	Clay.	Feldenheimer and Plowman: E.P. 164,808, July 14, 1921.
Synthesis of formaldehyde.	Quartz tubes.	G.P. 563,874, May 28, 1924.
Synthesis of formaldehyde.	Ni powder.	Foster and Schiazappa: (1926).
Synthesis of formaldehyde	$\text{Cu}$ .	Société National de Recherche pour le Traitement des Combustibles: P.P. 606,596, June 16, 1926.
Synthesis of formaldehyde.	Various contact substances.	Sabalitschka and Harnish: <i>Biochem. Z.</i> , <b>190</b> , 265-277 (1927).
Synthesis of formaldehyde; T. 130-200° at ordinary pressure.	Ni, Fe, Co, Cu, Pt, or their oxides.	Roman: P.P. 734,065, July 19, 1930.
Synthesis of formaldehyde.	Ce, Th, rare earths.	I. G. Farbenindustrie A.-G.: G.P. 550,933, Kl 12g, May 23, 1932.
Synthesis of formaldehyde (1 part methanol + 8-10 parts air); T. 300-325°; contact time 0.15-0.5 sec.	$\text{MoO}_3 + \text{V}_2\text{O}_5$ (30% $\text{MoO}_3 + 70\% \text{V}_2\text{O}_5$ ).	Bakelite Corporation: G.P. 575,596, Kl 12o, April 29, 1933.
Synthesis of formaldehyde.	Ag or Cu.	Klar: <i>Chemiker Ztg.</i> , <b>59</b> , 741-745, 836 (1935).

Table 7 (Continued).

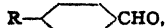
Reaction	Catalyst	Observer
Synthesis of formaldehyde from $O_3$ or $O_2$ and methane.	Mixture of oxides on quartz.	
Synthesis of formaldehyde from $O_3$ or $O_2$ and methane; 58% $CH_4$ +94.2% air; yield, 40%.	$Fe_2O_3+Cr_2O_3$ $Fe_2O_3+MnO_2$ $CuO+Cr_2O_3$ Alloy of Ag-Cu Ag+Cu	
Synthesis of formaldehyde.	Mixture of oxides on pumice or asbestos.	
Synthesis of formaldehyde.	Rhodium; rhodium+Ag+Cu.	

Table 8. Catalytic Synthesis of Acetaldehyde.

Reaction	Catalyst	Observer
Synthesis of acetaldehyde from acetylene.	Hg compounds.	Chemische Fabrik Griesheim Elektron: G.P. 360,417, Kl 12o, Gr. 7 Oct. 2, 1922. Lonza Elektrische Werke: F.P. 587,261, April 15, 1925. Shell Development Co. (Millar and Steck): U.S.P. 2,005,946, June 25, 1935.
Synthesis of acetaldehyde.	Phosphates, borates, silicates of groups 1, 2, 3, 4, or 7 of Mendeleeff System of elements; 25 p. $Zn(NO_3)_2$ precipitated with $NaOH$ +200 p. basic $CuCO_3$ ; $Zn(OH)_2$ +Cu formate; $MgO$ +Cu oxalate; $MgO$ +malachite.	I. G. Farbenindustrie A.-G.: Czechoslov. P. 36,717, July 10, 1931.
Synthesis of acetaldehyde.	Various oxides.	Kinsey and Adkins: <i>Ind. Eng. Chem.</i> , 24, 314-317 (1932).
Synthesis of acetaldehyde from alcohol; T. 300-500°.	Cu, Ag, or oxides of these metals.	Dreyfus: E.P. 389,134, April 6, 1933.
Synthesis of acetaldehyde by catalytic oxidation of alcohol.	$CaCl_2$ , $MgCl_2$ , $MgSO_4$ (free completely or partially from water of crystallization).	Dreyfus: E.P. 389,135, April 6, 1933. E.P. 742,274, March 3, 1933.
Synthesis of acetaldehyde.	Vapors of liquids which do not change during oxidation: benzene, petroleum, ether, acetone, isopropyl, butyl and isobutyl acetate.	Dreyfus: E.P. 389,145, April 6, 1933.
Synthesis of acetaldehyde from acetylene with $H_2SO_4$ .	Hg.	American Cyanamid & Chemical Corporation (Falter): U.S.P. 1,935,627, Nov. 21, 1933.

Table 9. Catalytic Synthesis of Aldol and Benzaldehyde.

Reaction	Catalyst	Observer
Synthesis of aldol from acetaldehyde.	$Al(OH)_3$ , $Fe_2O_3$ , $Sb(OH)_3$ and $ZnO$ .	Bosechard Elektrische Werke G.m.b.H.: G.P. 400,310, Kl 12o, Aug. 7, 1924.
Synthesis of benzaldehyde from benzene+CO.	$AlCl_3$ in the presence of $CuCl_2$ and $HCl$ .	Bayer: G.P. 98,706 (1897). Küchler and Buß: G.P. 126,421 (1900). Boehringer: G.P. 281,212 (1913). Gelsenkirschner Bergwerke A.-G.: G.P. 403,489 (1921).
Preparation of aromatic aldehydes of the type:	Water-free $AlCl_3$ and catalyst $CuCl_2$ .	Dupont: F.P. 820,545, Nov. 13, 1937.



R=alkyl group, with 1-8 C atoms in the molecule by treating benzene with CO and an alkyl compound which may be condensed with benzene, e.g., alkyl halide, aliphatic alcohols or ether, olefins, alkyl borate, alkyl formate; likewise in the presence of  $HCl$ .

Table 10. Catalytic Synthesis of Formic Acid.

Reaction	Catalyst	Observer
Synthesis of formic acid.	$\text{CuCl}_2$ , $\text{Fe}_2\text{O}_3$ or pyrites, $\text{Cr}_2\text{O}_3$ , $\text{Li}_2\text{O}$ , $\text{NiO}$ , or $\text{CuO}$ .	Dubose: <i>Rev. prod. chim.</i> , <b>27</b> , 433-434 (1924).
Synthesis of formic acid; T. 325-900°; theoretical yield, 50% formic acid 69 p. CO (by volume) + 25 p. $\text{H}_2\text{O}$ (by volume).	Boryl phosphate on charcoal.	Dupont (Vail): U.S.P. 1,895,238, January 24, 1933.
Synthesis of formic acid; T. 325°; 700 atm. pressure; from 93% $\text{CO} + 7\% \text{U}_2$ , $\text{CO}_2$ , $\text{N}_2 + 20$ p. water vapor.	$\text{CaCl}_2$ , $\text{CaI}_2$ , $\text{NaBr}$ .	Dupont (Carpenter): U.S.P. 1,924,769, Aug. 29, 1933.

Table 11. Catalytic Synthesis of Acetic Acid and Glacial Acetic Acid and their Derivatives.

Reaction	Catalyst	Observer
Synthesis of acetic acid.	Mn salts.	Consortium für Elektrochemische Industrie: G.P. 305,550, Kl 12o, Gr 12, Jan. 18, 1914.
Synthesis of acetic acid from acetylene (direct); 130 p. $\text{C}_2\text{H}_2 + 80-100$ p. $\text{O}_2$ .	50 p. $\text{Hg}(\text{NO}_3)_2$ (hydrates $\text{C}_2\text{H}_2$ ) + 10 p. $\text{CeO}_2$ (oxidizes acetaldehyde).	Dreyfus: G.P. 409,947 (1925).
Synthesis of acetic acid from acetaldehyde.	Not noble metals treated with x-ray, radium.	Ellinger: G.P. 423,542, Kl 12g, Jan. 8, 1926.
Synthesis of o-phenylene acetic-propionic acid.	Pt oxide; Pt black.	Hiers and Adams: <i>Ber.</i> , <b>59</b> , 162 (1926).
Synthesis of acetic acid.	Catalyst prepared from acetyl sulfuric acid (30 p. $\text{SO}_2 + 246$ p. glacial acetic acid) + $\text{Hg}$ acetate.	Canadian Electrical Products Co., Ltd. (Skirrow and Morrison): E.P. 671,558, Dec. 14, 1929.
Synthesis of acetic acid from CO and methanol.	$\text{H}_3\text{PO}_4$ .	I. G. Farbenindustrie A.-G.: F.P. 679,647, April 15, 1930.
Synthesis of acetic acid.	Vanadium.	Pasquin: <i>Vancoram Rev.</i> , <b>2</b> , 87-89 (1931).
Synthesis of acetic acid from CO and methanol in the presence of $\text{H}_2\text{O}$ vapor; T. 300-400°, 100-300 atm. pressure; 5.7 mols $\text{CO}$ ; 4 mols $\text{H}_2\text{O}$ vapor; 1 mol methanol to acetic acid + methyl acetate; T. 395°; 200 atm. pressure.	W oxide (not below $\text{W}_2\text{O}_3$ ); $\text{W}_2\text{O}_3$ + nitrates of Be, Bi, Zn, Cu, Al, Ce, Th; 90.0 mols $\text{WO}_3$ + 0.3 mols $\text{Al}_2\text{O}_3$ + 10.0 mols Zn + 2.5 mols $\text{Bi}_2\text{O}_3$ .	Patterson: F.P. 738,805, Dec. 30, 1932.
Synthesis of glacial acetic acid from acetaldehyde by oxidation with $\text{O}_2$ (reaction with induction period).	Mn + Fe, Co, Cr or Cu.	Kagan and Morozow: <i>Zhur. Priklad. Khim.</i> , <b>5</b> , 400-472 (1932).
Synthesis of acetic acid anhydride.	Pb and Th or other metals and their alloys.	Dreyfus: F.P. 737,610 and F.P. 737,611, Dec. 14, 1932.
Synthesis of acetic acid by oxidation with $\text{O}_2$ ; yield 80% from methyl ethyl ketone mixture of 2 kg. acetone and 100 g. conc. acetic acid (diluent); T. 80-100°.	5 g. Mn acetate, Cu acetate; Co and Mn acetyl acetonate.	I. G. Farbenindustrie A.-G.: F.P. 751,160, Aug. 28, 1933.
Synthesis of glycol acetal; yield 67-73% (from $\text{C}_2\text{H}_4(\text{OH})_2$ and $\text{C}_2\text{H}_5$ ).	$\text{HgO}$ and $\text{BF}_3$ .	Vaughn and Nieuwland: <i>Proc. Ind. Acad. Sci.</i> , <b>42</b> , 131-133 (1933).
Synthesis of acetic acid from alcohol or acetaldehyde; T. below 400°.	8.36 p. $\text{CuO} + 22.8$ p. $\text{Cr}_2\text{O}_3$ (heated to sintering; grained, heated at 300° with $\text{H}_2$ ); catalyst layer 15 cm. in length and 2.7 cm. <sup>2</sup> cross-section.	Goldschmidt, Askenasy and Grimm: G.P. 565,476, Kl 12o, May 31, 1933.

$\text{K} - \text{CH}_2\text{OH} \xrightarrow{\text{cat.}} \text{K} - \text{CH} + \text{H}_2$   
 $\text{K} - \text{CHO} + \text{H}_2\text{O} \xrightarrow{\text{cat.}}$   
 $\text{K} - \text{CH}(\text{OH})_2 \rightleftharpoons \text{K} - \text{CH}(\text{OH})_2 + \text{cat.}$   
 $\text{K} - \text{CHO} \rightarrow \text{K} - \text{COOH} + \text{K} - \text{CH}_2\text{OH}$

Table 11 (Continued).

Reaction	Catalyst	Observer
Synthesis of acetic acid from $\text{CH}_3\text{OH}$ and $\text{CO}$ —40 : 1; T. 300–500°; use of water containing methyl alcohol (20% $\text{H}_2\text{O}$ ) (optimum) is suggested to improve the life span of the contact and to obtain more free acid and less methyl acetate because with 100% methanol about half of the acid formed is maintained as methyl acetate.	Active charcoal impregnated with $\text{H}_3\text{PO}_4$ ( $\text{H}_3\text{PO}_4$ loses fast its activity and it is believed to be due to the formation of meta phosphoric acid).	Singh and Krase: <i>Ind. Eng. Chem.</i> , <b>27</b> , 909–11 (1935).
Synthesis of trimethyl acetic acid.	Hydrogen halide on active charcoal.	Dupont (Larson): U.S.P. 1,995,930, March 26, 1935.
$\begin{array}{c} \text{H}_3\text{C} \\ \diagup \\ \text{H}_3\text{C}-\text{CH}-\text{CH}_2\text{OH}+\text{CO} \rightarrow \cdot \\ \diagdown \\ \text{H}_3\text{C} \end{array}$ $\begin{array}{c} \text{H}_3\text{C} \\ \diagup \\ \text{H}_3\text{C}-\text{C}-\text{COOH} \\ \diagdown \\ \text{H}_3\text{C} \end{array}$ <p>from 83.4% <math>\text{CO}</math> 12.1% <math>\text{H}_2\text{O}</math> 4.1% isobutanol 0.4% <math>\text{HCl}</math> T. 300°; 700 atm. pressure.</p>		
Synthesis of acetic acid from methanol and $\text{CO}$ ; T. 300–350°; 150 atm. pressure.	87% $\text{H}_3\text{PO}_4$ ; addition of 2% $\text{Cu}$ phosphate raises the yield to 45%.	Taylor: <i>Gas World</i> , <b>104</b> , No. 2696, April 4, 1936.

Table 12. Catalytic Synthesis of Propionic Acid.

Reaction	Catalyst	Observer
Synthesis of propionic acid from steam, $\text{CO}$ and olefinic hydrocarbons ( $\text{C}_2\text{H}_4$ ); 72% $\text{CO}+3\%$ $\text{C}_2\text{H}_4+25\%$ $\text{H}_2\text{O}$ vapor; according to equation: $\text{RR}'\text{C} : \text{CR}''\text{R}''' + \text{H}_2\text{O} + \text{CO} = \text{CHRR}' : \text{CR}''\text{R}''' \text{COOH}$ in which $\text{R}$ , $\text{R}'$ , $\text{R}''$ and $\text{R}'''$ represent $\text{H}$ or an alkyl radical; yield 75%; T. 325°; 700 atm. pressure; $\text{CH}_3\text{CH}_2\text{COOH}$ from $\text{C}_2\text{H}_4$ ; butyric acid, $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ from propylene, $\text{C}_3\text{H}_6$ ; valeric acid, $\text{C}_5\text{H}_{10}\text{O}_2$ from butylene, $\text{C}_4\text{H}_8$ ; T. 325°; 700 atm. pressure.	Volatile halides, such as $\text{HCl}$ ; boron phosphate; $\text{NH}_4\text{Cl}$ on active charcoal (1% aqueous solution $\text{NH}_4\text{Cl}$ , $\text{NH}_4\text{Br}$ , or $\text{NH}_4\text{I}$ ); $\text{CaCl}_2$ or $\text{ZnCl}_2$ on active charcoal; $\text{NaBr}$ or $\text{ZnCl}_2$ ; inorganic volatile acids or halides, such as chlorine on activated charcoal.	Dupont (Carpenter): U.S.P. 1,924,763, Aug. 29, 1933. Dupont (Larson): U.S.P. 1,924,764, Aug. 29, 1933. U.S.P. 1,924,765, Aug. 29, 1933. Dupont (Carpenter): U.S.P. 1,924,766, 1933. U.S.P. 1,924,767, 1933. U.S.P. 1,924,768, Aug. 29, 1933.
Synthesis of propionic acid from $\text{CO}$ and $\text{C}_2\text{H}_4$ ; T. 325°; 700 atm. pressure.	$\text{Mo}$ , $\text{P}$ , $\text{As}$ , $\text{W}$ , $\text{U}$ , $\text{Cr}$ , $\text{V}$ , $\text{Ti}$ , $\text{Zr}$ , $\text{B}$ , $\text{WO}_3$ or a mixture of $\text{MoO}_3 + \text{Cr}_2\text{O}_3$ ; silicic and molybdic acids + $\text{Cr}$ vanadate.	Dupont (Carpenter): U.S.P. 2,008,348, July 16, 1935. U.S.P. 1,924,768, Aug. 29, 1933.

Table 13. Catalytic Synthesis of Anhydrides of Monobasic Acids.

Reaction	Catalyst	Observer
Synthesis of acetanhydride and benzaldehyde to cinnamic acid (Perkin's synthesis).	$\text{Na}$ acetate.	Perkin: <i>J. Chem. Soc.</i> , <b>31</b> , 388 (1877).
Synthesis of acetanhydride: $2\text{CH}_3\text{CO}_2\text{H} \rightarrow (\text{CH}_3\text{CO})_2\text{O} + \text{H}_2\text{O}$	Alkali phosphates—sometimes as alloys: $\text{Fe}$ , $\text{Mn}$ , $\text{Ni}$ , $\text{Al}$ , $\text{Cu}$ .	I. G. Farbenindustrie A.-G.: G.P. 411,106 (1922). G.P. 417,731 (1921). B.P. 230,063 (1925). B.P. 269,166 (1927). U.S.P. 1,570,514 (1926).
Synthesis of propionic anhydride from vapors of ethylidene di-propionate at 350° by once passing through; 31% converted.	Silicic acid treated with phosphoric acid.	Boehringer und Söhne: F.P. 746,684, June 2, 1933.

Table 14. Catalytic Synthesis of Anhydrides of Dibasic Acids.

Reaction	Catalyst	Observer
Conversion of phthalic acid as well as the anhydride to benzoic acid + CO <sub>2</sub> (in the presence of H <sub>2</sub> O vapor).	Na <sub>2</sub> CO <sub>3</sub> , CaCO <sub>3</sub> , CuSO <sub>4</sub> .	I. G. Farbenindustrie A.-G.: G.P. 445,565 (1925). Dupont: U.S.P. 1,712,753 (1924).
Conversion of phthalic acid as well as the anhydride to benzene + 2CO <sub>2</sub> (in the presence of water vapor).	CdO + Al <sub>2</sub> O <sub>3</sub> .	I. G. Farbenindustrie A.-G.: E.P. 262,101 (1926).
Preparation of phthalic anhydride (C <sub>8</sub> H <sub>4</sub> O <sub>3</sub> ).	Vanadium catalysts.	Bergstrom, Gilkey and Lung: <i>Vancorom Rev.</i> , 3, 13-18 (1932).
Preparation of maleic anhydride (C <sub>4</sub> H <sub>2</sub> O <sub>3</sub> ); contact time from 0.1-0.25 sec.; T. 475-550°.	Metal oxides of the 3rd and 6th groups of the Periodic System; vanadium oxide activated through small amounts of activators from the group Al, Mg, Mg, Mo (hardly meltable porous carrier, such as Alundum).	National Aniline and Chemical Co., Inc. (Pannett): U.S.P. 1,895,522, Jan. 31, 1933.

Table 15. Catalytic Synthesis of Ketones.

Reaction	Catalyst	Observer
Synthesis of ketones.	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ; metal sulfates of Cr, Mn, Al, Ca, Ba, Sr, Mg and Ag.	Ketoid Co.: E.P. 237,573, Sept. 16, 1925.
Synthesis of ketones from carboxyl-free aliphatic compounds.	Porous carrier material charged with a metal oxide such as the oxide or carbonate of Co, Mn, Cr.	Holzverkohlung Industrie A.-G.: E.P. 315,818, Sept. 11, 1929.
Synthesis of unsaturated ketones from unsaturated volatile carbonic acids of the aliphatic or cyclo-aliphatic series or the derivatives of the latter; at elevated temperatures at which no cracking of unsaturated carbonic acids takes place and favoring catalysts over which water and CO <sub>2</sub> are split off from the organic compounds; unsaturated reaction compounds; acrylic acid, crotonic acid, abietinic acid and naphthenic acid.	Difficultly reducible metal oxides such as Al, Th, Mn, Ca, Ba, Sr, Cr, Ti; oxides or metals such as Fe, Cu, Co, Ni, or their alloys.	
Synthesis of aliphatic ketones from carboxyl free aliphatic compounds with at least 2 bound C atoms and water vapor at elevated temperature.	At least one metal oxide compound on a metallic carrier such as Fe sponge or a metal with a rough surface such as a metal oxide compound is united with a heavy metal oxide such as Fe or Mn oxide, also light metal oxides such as CaO or a mixture of same.	Holzverkohlung Industrie A.-G.: Swiss P. 140,705, Sept. 16, 1930.
Synthesis of oxygen-containing aliphatic organic compounds, such as carbonic acid, esters, alcohols, aldehydes and ketones.	Masses of a zeolite structure with K, Na, Li, V, Cr, Mo, Mn, Fe, Co, Ni, Ag, Cu, Zn, Cd, Pb, Bi, Sb, Ca, Sr, Ba and elements Be, Mg, Al, Ce as well as of the rare earths B, Si, Ti, Zr, Th, U, W.	Société de Chimie de la Grand Paroisse Azote et Produits Chimie: E.P. 343,807, March 19, 1931.
Synthesis of oxygen-containing organic compounds.		Dreyfus: F.P. 722,850, March 26, 1932.
Synthesis of oxygen-containing organic compounds.		Dupont (Larson): U.S.P. 1,844,857, Feb. 9, 1932.
Synthesis of ketones from aliphatic alcohols (except tertiary alcohols); T. 250-650°; diminished pressure.	Mixture of difficultly reducible metal oxides + readily reducible metal oxides + a metal halide.	Commercial Solvents Corporation (Bloomfield, Swallen and Crawford): Can. P. 321,645, April 19, 1932.
Synthesis of higher ketones from aliphatic alcohols.	Alkaline-earth oxides or MgO; alkali metal oxides to which are added other metals, their oxides or carbonates being known for their catalytic action.	Deutsche Gold- und Silber Scheideanstalt (Roessler): F.P. 747,385, Aug. 19, 1932.

Table 15 (Continued).

Reaction	Catalyst	Observer
Synthesis of higher ketones from aliphatic alcohols acting upon ketones, such as acetone at 150-400°; in vapor or liquid phase; reaction based upon an alkylation of used ketones: $\text{CH}_3\text{COCH}_3 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COC}_2\text{H}_5 + \text{H}_2\text{O}$ ; higher alcohols and ketones with a branched chain are formed, e.g., methanol and acetone are led at 230° in equimolecular amounts with a diluting gas, such as $\text{N}_2$ ; methyl-propyl and methyl-amyl ketones obtained from acetone, also butanol and higher ketones with 6 and 8 carbons in a molecule form methyl-ethyl ketone.	Alkaline-earth oxides including Mg, as well as metal oxides, such as Al oxide to which Cu, Ag, or metal oxides, such as $\text{MoO}_3$ are added; e.g., active alumina is impregnated with 15% Cu formate and 1.8% $\text{MoO}_3$ with additional treatment consisting of a mixture of air and $\text{H}_2\text{O}$ vapor.	Deutsche Gold- und Silber Scheideanstalt (Roessler): F.P. 741,385, Feb. 10, 1933.
* Synthesis of acetone from $\text{C}_2\text{H}_5$ and $\text{H}_2\text{O}$ vapor: (1) $\text{C}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO} + 36.0 \text{ Cal.}$ (2) $\text{CH}_3\text{CHO} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COCH}_3 + 2\text{H} + \text{CO}_2 + 17.5 \text{ Cal.}$ T. 425-450°.	Basic Zn vanadate; $2\text{ZnO} \cdot \text{V}_2\text{O}_5$ ; less active; basic Cd vanadate and Fe oxide (Zn vanadate in contrast to Cd vanadate may be regenerated by blowing through air at 350-500°).	Platonow, Plakidina and Weltistow: <i>Zhur. Obshchei Khim.</i> 4 (66), 421 (1934).
Synthesis of ketones from <i>sec.</i> alcohol, isopropanol, and water (12%); T. 550-700°; led with 100-105% of theoretically required amt. of air; <i>sec.</i> butyl alcohol, amyl alcohol, diisopropyl carbinol or alcohols obtained by catalytic hydrogenation of CO may be oxidized to ketones.	Ag.	Imperial Chemical Industries, Ltd. (Woolcock): U.S.P. 2,015,094, Sept. 24, 1935.
Synthesis of ketones from aliphatic alcohols, e.g., high molecular, especially hexyl, alcohols (usual ketonization conditions).	60% Cu, 38.5% Zn and 1.5% Sn, or 60% Cu, 10% Zn, 25% Ni, 3% Sn and 2% Fe.	Standard Alcohol Co. (Archibald and Beamer): U.S.P. 2,028,267, Jan. 21, 1936.
Synthesis of alicyclic ketones from corresponding secondary alicyclic alcohols and 0.25-0.5 mol $\text{O}_2$ or air; T. 300-315°; likewise in the presence of $\text{H}_2\text{O}$ ; T. 500-600°; e.g., cyclohexanol to cyclohexanone; yield 50%; 45% unchanged cyclohexanol and 5% CO and $\text{CO}_2$ ; menthol to menthone; borneol to camphor; tetrahydro- $\beta$ -naphthol to tetrahydro- $\beta$ -naphthone.	Ag catalysts.	Dupont (deWitt Graves):
Preparation of ketones from monocarbonic acid or its ester in the vapor phase; e.g., 60 g. caprylic acid is led through a glass tube 1½ in. in diameter (heated electrically) over 250 cc. melted quartz and 145 cc. of the catalyst; T. 400-415°; yield, greater than 99% caprylone; the solid white mass obtained is treated with $\text{Na}_2\text{CO}_3$ solution and recrystallized from 80% alcohol; likewise, a mixture of one mol lauric and 2 mols butyric acids are converted into pentadecanone-4-laurone and dipropyl ketone.	Mn or Zn chromite prepared from a solution of $(\text{NH}_4)_2\text{CrO}_4$ obtained by neutralizing 300 g. $\text{Cr}_2\text{O}_3$ with 398 cc. 28.5% $\text{NH}_4\text{OH}$ made up to 1.5 l. is introduced into a solution obtained by 1077 g. of a 50% Mn nitrate solution made up to 1.5 l., adding more than 154 cc. of a 28.5% $\text{NH}_4\text{OH}$ solution, filtering, heating first to 110° and then to 400°, whereby $\text{Mn-NH}_4$ chromate is decomposed to Mn chromite; to the granulated and screened chromite is added 2% graphite, and the mixture is pressed into tablets ¾ in. in thickness.	Dupont (Wirtz): U.S.P. 2,108,156, Feb. 15, 1938.

Table 16. Catalytic Synthesis of Amino-Compounds.

Reaction	Catalyst	Observer
Synthesis of diamino butane; 1d,1,1,2-diamino butane; 1,2-diamino-2-methyl propane (d,1,1,2-diamino propane).	Pd most active for hydrogenation.	Strack and Schwaneberg: <i>Ber.</i> , 66, 330-333, Sept. 13, 1913.

Table 16 (Continued).

Reaction	Catalyst	Observer
Synthesis of aromatic amines from oxy compounds of the benzene series and $\text{NH}_3$ under increased temperature and pressure; the process with $\text{Al}(\text{OH})_3$ proceeds without formation of secondary amines; a large excess of $\text{NH}_3$ , and temp., $450^\circ$ .	Best results with $\text{Al}(\text{OH})_3$ as catalyst (acts for a long time).	I. G. Farbenindustrie A.-G. (Herald and Reubold): G.P. 570,365, Kl 12g, Feb. 15, 1933. E.P. 378,373, March 31, 1932. F.P. 708,202, July 21, 1931.
Synthesis of di-orthocarboxyl phenyl amine anthraquinone by heating the di-halogen anthraquinone with anthranilic acid or its salts in low-boiling alcohols under pressure up to $135\text{--}140^\circ$ .	Cu.	Dupont (Rintelman and Goodrich): U.S.P. 1,841,674, Jan. 19, 1932.
Synthesis of methylamine ( $\text{MeNH}_2$ ) from $\text{Me}(\text{OH})$ and $\text{NH}_3$ ; the gaseous mixture is introduced at an intermediate point in a fractionating column; liquid $\text{Me}(\text{OH})$ is passed down the column and gaseous $\text{MeNH}_2$ up the column; the resulting $\text{MeOH}$ solution of $\text{MeNH}_2$ is recovered from the bottom of the column.		Commercial Solvents Corporation (Swallen): Can. P. 326,718, Nov. 10, 1932.
Synthesis of amines from an alcohol.	P-containing catalysts, such as $\text{P}_2\text{O}_5$ , phosphoric acid and phosphates are used.	Rohm and Haas Co.: F.P. 734,404, March 30, 1932.
Synthesis of aromatic amines, such as aniline at high temp. and pressure from a halogenated aromatic hydrocarbon such as $\text{PhCl}$ and an aqueous $\text{NH}_3$ solution.	Cuprous compound (maintained in this state).	Dow Chemical Co. (Putnam): U.S.P. 1,885,625, Jan. 11, 1932.
Preparation of amines from alcohols and ammonia: 8 g. $\text{CH}_3\text{OH}$ and 10 g. $\text{NH}_3$ led over a catalyst form monomethylamine and dimethyl ether; contact time for gases, 2.2–2.3 sec.	Al salts of oxy-acids of Si or P; kaolin heated to $460^\circ$ ; $\text{AlPO}_4$ .	National Aniline and Chemical Co., Inc. (Punnett): U.S.P. 2,113,241, April 5, 1938.
Preparation of amines from trialkyl amines and ammonia: (1) 2 mols trimethylamine and 1 mol liquid ammonia (100% in excess) heated in an iron vessel; time, 24 hrs.; dimethylamine and a small amount of monomethylamine formed; (2) triethylamine and ammonia heated in an autoclave; T. $150^\circ$ ; monoethylamine and diethylamine formed; (3) tributylamine and ammonia passed over silica gel impregnated with $\text{Al}_2\text{O}_3$ ; T. $400^\circ$ ; monobutylamine and dibutylamine formed.	Ni; Al silicate.	DuPont (Millington): U.S.P. 2,112,970, April 5, 1938.
Reaction between $\alpha$ -naphthol and <i>p</i> -phenylenediamine to form indophenol; indophenol formation takes place in solution as well as on the surface of charcoal.	$\text{H}_2\text{O}_2$ or charcoal + oxygen of air (KCN and amyl alcohol act as poisons).	O'Brien, Tkac and Schwab: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 2480–2483 (1938).
Preparation of primary amines from propyl-, butyl-, and amyl alcohol by subjecting them in the form of fine droplets or thin films at high temperatures and pressures to the action of $\text{NH}_3$ or amines, e.g., a mixture of butanol and a metal catalyst is dispersed in $\text{NH}_3$ atmosphere at $200\text{--}300^\circ$ and $42\text{--}84 \text{ kg/cm}^2$ , and the primary butylamine originating is removed continuously from the reaction space.	Catalysts may be used.	Kodak, Ltd.: F. P. 834,372, Nov. 18, 1938.

Table 16 (Continued).

Reaction	Catalyst	Observer
Preparation of tertiary aliphatic amines by leading vapors of aliphatic aldehydes with not more than 6 carbon atoms, and of secondary aliphatic amines, the alkyl groups of which contain not more than 6 carbon atoms together with H <sub>2</sub> over hydrogenation catalysts, e.g., if on one hand 8 g. acetaldehyde are evaporated in 8 g. H <sub>2</sub> and on the other hand 28 g. diethylamine in 1 g. H <sub>2</sub> combining both gas streams at 120° and leading them at the same temperature over the catalyst, cooling the reaction product with water and then with solid CO <sub>2</sub> , a yield of 90% triethylamine is obtained; in a similar manner, dibutylamine with butyraldehyde is converted into tributylamine and with acetaldehyde into ethyldibutylamine (critical point 172-175°).	Ni.	I. G. Farbenindustrie A.-G.: G.P. 673,017, Kl 12g, March 14, 1939; add to G.P. 489,551; (Refer to C. 1931 I 1823).
Synthesis of $\alpha$ - and $\beta$ -amino derivatives of the anthraquinone series; halogen anthraquinone is heated with aqueous NH <sub>3</sub> in an autoclave under pressure.	Oxyhalogen compound, such as KIO <sub>3</sub> or NaBrO <sub>3</sub> and NH <sub>4</sub> NO <sub>3</sub> ; Cu(NO <sub>3</sub> ) <sub>2</sub> , CuO, or AgCl may also be used.	Groggins: U.S.P. 1,923,618, Aug. 22, 1933.
Synthesis of aliphatic amines from alcohols and NH <sub>3</sub> ; mixtures of mono-, di- and tributylamine are obtained from butanol and mixtures of methyl amines from methanol.	Al <sub>2</sub> O <sub>3</sub> , ThO <sub>2</sub> , B <sub>2</sub> O <sub>3</sub> , WO <sub>3</sub> and TiO <sub>2</sub> precipitated upon gels (silica gel, Al <sub>2</sub> O <sub>3</sub> gel, Cr <sub>2</sub> O <sub>3</sub> gel) in a conc. of about 20%.	Dupont: E.P. 384,714, Jan. 5, 1933.
Synthesis of oxy-alkyl amines from oxy-acid nitriles in which the oxy- and the CN groups are not bound to the equal C atom; they are heated with H <sub>2</sub> in a liquid phase; from ethylene cyanhydride in the presence of a catalyst a mixture is obtained at 50 atm. and at 60-70°; from $\beta$ -oxybutyric acid nitrile, mono- and tri- (3-oxybutyl) amines are formed; primary oxyalkylamine formation is favored by hydrogenation in the presence of aqueous solutions of NaCl or NH <sub>4</sub> .	Ni; kieselguhr contact.	I. G. Farbenindustrie A.-G. (Schlichting): G.P. 573,983, Kl 12g, April 8, 1933.
Synthesis of N <sub>2</sub> ring compounds.	Ni.	Winans and Adkins: <i>J. Am. Chem. Soc.</i> , <b>55</b> , 4167-76 (1933).
Separation of trimethylamine and NH <sub>3</sub> ; both bases together with air are led over the catalyst yielding mono- and dimethyl amines; T. 300-500°.	Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .	Rohm and Haas Co. (Andrews and Washburne): U.S.P. 2,095,786, Oct. 12, 1937.
Synthesis of diethylamine from NH <sub>3</sub> and alcohol; T. 350 $\pm$ 10° passage 0.6-0.71 of gaseous alcohol per minute; yield of all amines, 30-40%, 60-80% of which is diethylamine.	Al <sub>2</sub> O <sub>3</sub> · SiO <sub>2</sub> (dehydrating catalysts); the catalyst may be regenerated after 25-30 hours of operation either with water vapor at 350° or with nitrogen oxides at 300°.	Opotzki and Dranowski: <i>Ukrain. Khim. Zhur.</i> , <b>11</b> , 446-459 (1938).

Table 17. Catalytic Synthesis of Nitriles.

Reaction	Catalyst	Observer
Synthesis of nitriles.	Silicic acid gel.	Mitchell and Reid: <i>J. Am. Chem. Soc.</i> , <b>53</b> , 321-330 (1931).
Synthesis of cyclic nitriles by catalytic cyanation of cyclic hydrocarbons and phenol ethers; the nucleus condensation of cyclic compounds with CCl <sub>3</sub> CN has been perfected.	KOH is added at the C : N bond of the KC( : NH)CCl <sub>3</sub> and the resulting unstable asymmetrical KC(NH <sub>2</sub> )OKCCl <sub>3</sub> converted spontaneously into CHCl <sub>3</sub> and a pseudo-amide alkali compound KC( : NH)OH which breaks down into KCN and KOH, the latter then reacting with another molecule of KC( : NH)CCl <sub>3</sub> .	Houben and Fischer: <i>Ber.</i> , <b>66B</b> , 339-349 (1933).



Table 17 (Continued).

Reaction	Catalyst	Observer
Synthesis of mandelic acid nitriles.		Brick: <i>J. Am. Chem. Soc.</i> , <b>55</b> , 2593-2597 (1933).
Synthesis of nitriles by passing $\text{EtCO}_2\text{H}$ and $\text{NH}_3$ through heated catalysts, T. $400^\circ$ , at the rate of 0.2229 min. and 220-40 cc./min.	(1) Japanese acid clay; (2) $\text{SiO}_2$ gel; (3) $\text{Al}_2\text{O}_3$ ; yields of $\text{PrCN}$ : with (1)—95.5 % with (2)—80.16 % with (3)—85.9 %	Abe: <i>Waseda Applied Chem. Soc. Bull.</i> , <b>19</b> , 8-14 (1933).
Synthesis of acetonitrile.	Japanese acid earth.	Kobagashi and Abe: <i>J. Soc. Chem. Ind. Japan</i> , <b>36</b> , 42B-43B (1933).
Synthesis of nitriles: dimethyl ether + $\text{HCN}$ or substances converting it to acetonitrile, T. $290^\circ$ ; 88-93% $\text{HCN}$ converted into acetonitrile; formamide + $\text{HCN}$ to propionitrile; T. $320^\circ$ .	Granulated $\text{Al}(\text{OH})_3$ (peptized $\text{Al}_2\text{O}_3$ 360 l./hour/l. $\text{Al}_2\text{O}_3$ ).	I. G. Farbenindustrie A.-G.: F.P. 799,091, June 5, 1936.
Synthesis of nitriles from fatty acids with at least 6 C atoms, such as stearic acid and gaseous $\text{NH}_3$ ; T. $250$ - $350^\circ$ .	Dehydrating catalysts.	Armour & Co. (Ralston, Pool and Harwood): U.S.P. 2,061,314, Nov. 17, 1936.
Synthesis of unsaturated aliphatic or cyclo-aliphatic carboxy acid nitriles from saturated halogen-containing carboxy-acid nitriles, e.g., nitriles of halogenated propionic, butyric, palmitic, or naphthenic acids; T. greater than $100^\circ$ ; T. $300$ - $450^\circ$ under diminished pressure; a chlorination product of isobutyronitrile consisting of the monochloride of isobutyronitrile and a mixture of the nitrile of methacrylic acid and chlorisobutyronitrilene was obtained; T. $400$ - $450^\circ$ .	Hydrogen halide; silicic acid gel, $\text{Ti}$ oxide, $\text{Al}$ oxide, $\text{BaCl}_2$ or active charcoal.	I. G. Farbenindustrie A.-G.: F.P. 794,255, Feb. 12, 1936.
Synthesis of urea from cyanamide (conc. solution treated with $\text{H}_2\text{SO}_4$ ).	$\text{TiO}_2$ .	Wohler: (more than 100 years ago).
Synthesis of urea from $\text{CO}_2$ and ammonia. $2\text{NH}_3 + \text{CO}_2 \rightleftharpoons \text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O}$ T. $135$ - $150^\circ$ ; pressure 50-100 atm. $(\text{NH}_4)_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{NH}_4\text{COONH}_4 \rightarrow \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O}$	Without catalyst.	Badische Anilin u. Soda Fabrik: E.P. 145,060 (1920). E.P. 182,331 (1921). U.S.P. 1,429,483, Sept. 19, 1922. U.S.P. 1,429,953, 1922.
Synthesis of urea from $\text{CO}_2$ and ammonia; $\text{CO}_2$ passed over ammonium compounds.	$\text{NH}_4\text{Cl}$ or $\text{CaCl}_2$ .	Norsk. Hydro-Elektrisk Kvaelfabrik: Norwegian P. 39,747 (1922).
Preparation of urea by reaction between $\text{Fe}(\text{CO})_5$ and dry $\text{NH}_3$ in the gaseous state, using a 1500-watt lamp or sunlight; a small yield obtained; course of the reaction: (1) $\text{Fe}(\text{CO})_5 + \text{NH}_3 \rightarrow \text{Fe}(\text{CO})_4\text{NH}_3$ (2) $2\text{Fe}(\text{CO})_4\text{NH}_3 \rightarrow \text{CO}(\text{NH}_2)_2 + \text{H}_2\text{Fe}(\text{CO})_4 + \text{Fe}(\text{CO})_5$ (3) $2\text{H}_2\text{Fe}(\text{CO})_4 \rightarrow 2\text{H}_2 + \text{Fe}(\text{CO})_5 + \text{Fe}(\text{CO})_4$	Silicic acid aerogel accelerates the reaction.	Fedorov and Talmud: <i>Acta Physicochim. U.R.S.S.</i> , <b>8</b> , 205-210 (1938).

Table 18. Catalytic Synthesis of Benzene.

Reaction	Catalyst	Observer
Synthesis of benzene.	Ni.	Fischer and Meyer: <i>Brennstoff-Chem.</i> , <b>12</b> , 225 June 15, 1931. Fischer and Kuster: <i>Ibid.</i> , <b>14</b> , 3-8 (1933). Fischer and Pichler: <i>Ibid.</i> , <b>14</b> , 306-310 (1933).
Synthesis of benzene.	Fe, Ni, Co; for Cu-containing contact, no preliminary reduction necessary; Co contact (reduction temperature, $350$ - $400^\circ$ ).	Fischer and Koch: <i>Ibid.</i> , <b>13</b> , 428-434 (1932); 61-68 (1932).

Table 18 (Continued).

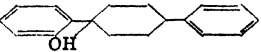
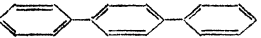
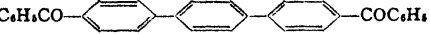
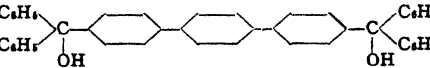
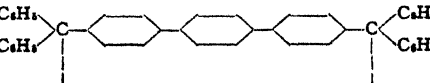
Reaction	Catalyst	Observer
Synthesis of benzene from CO and H <sub>2</sub> at ordinary pressure; CO : H = 1 : 1; T. 210°.	Highly porous Co, Cu, Th, U (8 : 1 : 0.15 : 0.15) made up in the form of their nitrates plus starch; U exceeds Th in polymerization action; Ni activated by ThO <sub>2</sub> and UO <sub>2</sub> ; small additions of K <sub>2</sub> CO <sub>3</sub> or Rb <sub>2</sub> CO <sub>3</sub> favorable; Ni + 18% ThO <sub>2</sub> (UO <sub>2</sub> ) Ni oxalate + UO <sub>2</sub> (no effect); for ThO <sub>2</sub> (108 cc./cc., C <sub>6</sub> H <sub>6</sub> ) for UO <sub>2</sub> (89 cc./cc., C <sub>6</sub> H <sub>6</sub> ).	Fujimura: <i>J. Soc. Chem. Ind. Japan</i> , <b>35</b> , 179B-182B (1932); <b>36</b> , 413B-416B (1933); <b>36</b> , 119B-121B (1933).
Synthesis of benzene.	Alloy skeletons.	Fischer and Meyer: <i>Brennstoff-Chem.</i> , <b>15</b> , 84-93, 107-110 (1932).
Synthesis of benzene CO : H = 33.1 : 64.7; velocity passage 246; T. 197°; T. 300-500° (0.5 g.).	Co : Cu : ThO <sub>2</sub> = 9 : 1 : 2 (1 g. contact).	Watanabe, Morikawa and Igawa: <i>J. Soc. Chem. Ind. Japan</i> , <b>38</b> , 70B-73B (1935).
Synthesis of benzene T. 200-450°; cooled in CO <sub>2</sub> stream.	NiO + 10% Al <sub>2</sub> O <sub>3</sub> + 20% MnO (precipitate of nitrates with K <sub>2</sub> CO <sub>3</sub> ).	Oscherowa: <i>Russ. P.</i> <b>47</b> , 287, June 30, 1936.
Synthesis of benzene.	Fe, Co, Ni mixed catalysts.	Kita: <i>J. Fuel Soc. Japan</i> , <b>16</b> , 60-62 (1937).
Synthesis of benzene from CO and H <sub>2</sub> under ordinary pressure.	Fresh catalysts, after their reduction with H <sub>2</sub> , may be activated through a slow oxidation with the oxygen of air (treatment with air for space velocities under 2600 resulted in an improvement of the activity by 8-10%; however, regenerated catalysts do not show an increase in activity by this pre-treatment).	Katayama, Murata, Koide and Tsuneoka: <i>Sci. Papers Inst. Phys. Chem. Research (Tokyo)</i> , <b>34</b> , 1181-95 (1938).
Synthesis of bi-radicals through a series of catalytic processes following in sequence, for example, I. 1,4-cyclohexandion, and II. lithium phenyl are converted into:		Muller and Sok: <i>Ber.</i> , <b>70</b> , 1990-1992 (1937).
III. 		
This is dehydrogenated over Se. the catalyst forming:		
IV. 		
This is converted with benzoyl AlCl <sub>3</sub> chloride into:		
V. 		
This is converted with lithium phenyl into:		
VI. 		
In the presence of a catalyst, the corresponding chloride of VI. gives a dark red biradical, which is very sensitive to light.	Cu powder.	
VII. 		

Table 19. Synthetic Processes of Industrial Significance.

Reaction	Catalyst	Observer
Preparation of highly viscous oils (lubricants) with high flash point from gases rich in low olefins, ethylenes, propylene, butylene and amylene at 200° under ordinary or high pressure.	Al, Zn, or Fe chlorides.	I. G. Farbenindustrie A.-G.: E.P. 299,086, Nov. 15, 1928.
Preparation of synthetic lubricants; diphenyl oxide heated at 700° under pressure; 5% gaseous low-boiling substances and 20% tarry ingredients; 75% of oil, b.p. 200–350° and $D_{25} = 1.12$ –1.21; resembles the hydrocarbon of the crude oil and is used as a lubricant.	Mixture of $Al_2O_3$ and CuO.	Dow Chemical Co. (Gräbe and Stoesser): U.S.P. 1,905,850, April 24, 1933.
Synthesis of anthraquinone obtained from benzene and phthalic anhydride; theoretical yield of <i>o</i> -benzoyl-benzoic acid.	Al (2 g. atoms) and $HgCl_2$ (2 g. molecules).	Gallay and Whitby: <i>Can. J. Research</i> , 2, 31 (1930).
Esterification; preparation of isoamyl acetate by leading a mixture of alcohol and 99% acetic acid over the catalyst; T. 100–120°, yield 83–78% by increasing the passage velocity from 0.15 to 4.0 ccm./min., the yield did not drop markedly.	$H_3PO_4$ impregnated on active charcoal.	Turowa-Poljak and Worotnikowa: <i>Zhur. Priklad. Khim.</i> , 11, 643–45 (1938).
Preparation of mixed tertiary ethers from tertiary olefins and primary or secondary alcohols in the presence of a catalyst, e.g., isobutyl- <i>tert</i> -butyl ether, isoamyl- <i>tert</i> -butyl ether, <i>sec</i> -butyl- <i>tert</i> -butyl ether, methyl- <i>tert</i> -hexyl ether, all of them alone or in mixture with other substances serve as solvents for lacquers, resins, and as extraction agents for organic substances.	$H_2SO_4$ .	Shell Development Co. (Evans, Th. and Edlund): U.S.P. 2,139,359, Dec. 6, 1938.

## PART IV

## Catalytic Decomposition in Inorganic Chemistry

Table 1. Catalytic Decomposition of Ammonia.

Reaction	Catalyst	Observer
Decomposition of $NH_3$ .	Fe.	Despretz (1829). Tenar (1813).
Decomposition of $NH_3$ .	Au (decomposes to nitrogen suboxide).	Hinshelwood and Richard: <i>Proc. Roy. Soc. London (A)</i> , 108, 211–215 (1924).
Decomposition of $NH_3$ .	Mo wire.	Burk: <i>Proc. Nat. Acad. Sci. U.S.</i> , 13, 67–74 (1926).
Decomposition of $NH_3$ .	Ni.	Elöd and Bauholzer: <i>Z. Elektroch.</i> , 32, 355–58 (1926).
Decomposition of $NH_3$ .	Ni, Mo, W.	Kunsman: <i>J. Am. Chem. Soc.</i> , 50, 2110–13 (1928).
Decomposition of $NH_3$ .	Activated Fe.	Kunsman, Lamar and Deming: <i>Phil. Mag.</i> (7), 10, 1015–37 (1930).
Decomposition of $NH_3$ .	W wires heated to 950–1150° at 37 mm. pressure.	Dixon: <i>J. Am. Chem. Soc.</i> , 53, 1763–1773 (1931).
Decomposition of $NH_3$ .	Cu.	Hailes: <i>Trans. Faraday Soc.</i> , 27, 601–606 (1931).
Decomposition of $NH_3$ .	$SnO_2 + Sb_2O_3 + Pt$ ; CaO, $SiO_2$ , $SnO_2$ , $V_2O_5$ .	Adadurow and Sokolow: <i>Zhur. Priklad. Khimii</i> , 4, 191–200 (1931).

Table 1 (Continued).

Reaction	Catalyst	Observer
Decomposition of $\text{NH}_3$ .	W powder, particle size $10^{-4}$ mm.	Frankenburger and Hodler: <i>Trans. Faraday Soc.</i> , <b>28</b> , 229-442 (1932).
Decomposition of $\text{NH}_3$ .	Os surface.	Arnold and Burk: <i>J. Am. Chem. Soc.</i> , <b>54</b> , 23-32 (1932).
Decomposition of $\text{NH}_3$ .	Grained $\text{Fe} + \text{Al}_2\text{O}_3$ or $\text{MgO}$ .	Dupont Ammonia Corporation: F.P. 363,300, Jan. 7, 1932.
Decomposition of $\text{NH}_3$ .	$\text{Fe} + \text{Al}_2\text{O}_3$ .	Gedye and Allitone: <i>J. Chem. Soc.</i> , <b>1932</b> , 1158-1160, 1160-1169, 1169-1172.
Decomposition of $\text{NH}_3$ .	Contact consisting of oxides: $\text{Al}_2\text{O}_3$ , $\text{ZrO}_2$ , $\text{Cr}_2\text{O}_3$ , $\text{MgO}$ , $\text{CaO}$ .	Imperial Chemical Industries, Ltd.: F.P. 387,318, March 2, 1933.
Decomposition of $\text{NH}_3$ .	Fe wire (catalytic activity changes abruptly; smaller for higher temperature).	Fischbeck and Salzer: <i>Z. Elektroch.</i> , <b>41</b> , 158-169 (1935).
Decomposition of $\text{NH}_3$ .		Chrisman: <i>Zhur. Fiz. Khimii</i> , <b>7</b> , 931-38 (1936).
Decomposition of $\text{NH}_3$ ; initial pressure 180 mm.; T. 360-575°; the kinetics of the catalytic reaction is expressed by the empirical equation:	$\text{Fe-Al}_2\text{O}_3\text{-K}_2\text{O}$ .	Chrisman and Awaliani: <i>Visti Ukrain. Nauk. Doslidchogo Inst. Fis. Khem.</i> , <b>5</b> , 49-57 (1936). Kunsman: (Refer to C. 1929 I 2268).
$dP_{\text{NH}_3}/dt = (K \cdot P_{\text{NH}_3}^2 / P_{\text{H}_2}^2)^{1/2}$ <p>the activation energy <math>E_{360-575} = 11.7</math> k.cal./mol The results differ greatly from those obtained by Kunsman.</p>		
Decomposition of $\text{NH}_3$ ; (dry $\text{NH}_3$ is led over promoted Fe at 350-400°; T. 410° (stoichiometric amounts of $\text{N}_2$ and $\text{H}_2$ ascertained only at 410°; at 350° and below, only $\text{N}_2$ with traces of $\text{H}_2$ is set free); the comparison with ordinary Fe showed that the nitride slows down the reaction.	Fe nitride (promoted) (together with Frankenburger, it is assumed that Fe itself and not its nitride is the catalyst); mixed crystal (Fe-Fe nitride).	Chrisman and Kornitschuk: <i>Visti Ukrain. Nauk. Doslidchogo</i> , <b>6</b> , 95-101 (1936).

Table 2. Catalytic Decomposition of Hydrogen Peroxide.

Reaction	Catalyst	Observer
Decomposition of $\text{H}_2\text{O}_2$ .	Pt.	Thénard: <i>Jahresberichte</i> , <b>1</b> , 26 (1820/22).
Decomposition of $\text{H}_2\text{O}_2$ .	Ag powder is converted in catalysis into $\text{Ag}_2\text{O}$ .	Berthelot: <i>Bull. soc. chim.</i> , (2), <b>34</b> , 135 (1880).
Decomposition of $\text{H}_2\text{O}_2$ .	An Ag layer 0.0002 mm. thick deposited on glass; water.	Lemoine: <i>Compt. rend.</i> , <b>155</b> , 15 (1912); <b>155</b> , 9 (1912).
Decomposition of $\text{H}_2\text{O}_2$ .	Small amounts of alkali (velocity almost proportional to conc. of alkali).	Lemoine: <i>Compt. rend.</i> , <b>161</b> , 47 (1915).
Decomposition of $\text{H}_2\text{O}_2$ .	Colloidal Pd.	Rocasolano: <i>Compt. rend.</i> , <b>190</b> , 1502 (1918).
Decomposition of $\text{H}_2\text{O}_2$ .	Fertilized earth.	Osugi: <i>Ber. Inst. Landw. Forsch.</i> , <b>2</b> , 197-218 (1922).
Decomposition of $\text{H}_2\text{O}_2$ .	Blood charcoal.	Firth and Watson: <i>Trans. Faraday Soc.</i> , <b>19</b> , 601-610 (1924).
Decomposition of $\text{H}_2\text{O}_2$ .	Au hydrosol.	Galecki and Binner: <i>Bull. intern. acad. polon. sci.</i> , 93-127 (1925).
Decomposition of $\text{H}_2\text{O}_2$ .	Hg, Fe, Zn, Mg, Cu, Pb, Sb, K, Na, Ca and their compounds.	Floresco: <i>Bull. faculte Stiinte Gernanti</i> , <b>2</b> , 184-192 and 308-19 (1925).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{CuO}$ .	Quartaroli: <i>Gass. chim. ital.</i> , <b>55</b> , 619-638 (1925).

Table 2 (Continued).

Reaction	Catalyst	Observer
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{K}_2\text{Cr}_2\text{O}_7$ .	Robertson: <i>J. Am. Chem. Soc.</i> , <b>48</b> , 2072 (1926).
Decomposition of $\text{H}_2\text{O}_2$ .	Catalase and haemin.	Josephson: <i>Svensk Kem. Tid.</i> , <b>39</b> , 178-87 (1927).
Decomposition of $\text{H}_2\text{O}_2$ .	Mineral water with high content of $\text{Fe}''$ and $\text{Mn}''$ ions.	Gaisser: <i>Z. anorg. Chem.</i> , <b>41</b> , 401-407 (1927).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{Fe}$ ions (neutral salt action).	Kiss and Lederer: <i>Z. physik. Chem.</i> , <b>129</b> , 186-198 (1927).
Decomposition of $\text{H}_2\text{O}_2$ .	Colloidal Pt.	Heath and Walton: <i>J. Phys. Chem.</i> , <b>37</b> , 977 (1933).
Decomposition of $\text{H}_2\text{O}_2$ .	Active charcoal (Sufranorit and Appula).	Tartar and Schaffer: <i>J. Am. Chem. Soc.</i> , <b>50</b> , 2604 (1928).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{Cu}(\text{CH}_3\text{COO})_2$ , $\text{Mn}$ and $\text{Pb}$ acetate (weak action); cobalt acetate, strong action.	Mazzacholi and Vareton: <i>Ann. chim. applicata</i> , <b>19</b> , 415-420 (1929).
Decomposition of $\text{H}_2\text{O}_2$ .	Ferric salt + cupric salt; $(\text{Cu}(\text{OH})_2 + \text{Fe}(\text{OH})_2)$ .	Ostwald and Erbring: <i>Kolloid-Z.</i> , <b>57</b> , 7-14 (1931).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{I}'$ , $\text{CdI}$ and $\text{CdI}_2'$ influence the decomposition of $\text{H}_2\text{O}_2$ ; while $\text{Cd}''$ , $\text{CdI}_2$ do not; $\text{CdI}'$ decomposes $\text{H}_2\text{O}_2$ half as fast as $\text{I}'$ .	Charmadarjan and Alexejew: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>62</b> , 1677-1683 (1930).
Decomposition of $\text{H}_2\text{O}_2$ .	Colloidal $\text{Fe}(\text{OH})_2$ .	Spitalski and Konowalowa: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>62</b> , 1033-1043 (1930).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{CuSO}_4$ (strongly diluted), 1 g. $\text{Cu}$ per 10-1000 liters (less active than $\text{Cu}$ peroxide).	Gooding and Walton: <i>J. Phys. Chem.</i> , <b>35</b> , 3612-17 (1931).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{Cu}(\text{OH})_2$ (obtained from basic $\text{Cu}$ nitrate and $\text{Cu}$ oxalate).	Teletow and Alexejewa: <i>Ukrain. Khim. Zhur.</i> , <b>6</b> , No. 1, 61-73 (1931).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{OsO}_4$ (0.000001/liter and even higher dilution); maximum velocity with 0.001-0.005 <i>N</i> .	Quartaroli: <i>Gazz. chim. ital.</i> , <b>61</b> , 466-478 (1931).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{Fe}$ ions.	Kohlschütter: <i>Helv. Chim. Acta</i> , <b>14</b> , 1215-1246 (1931).
Decomposition of $\text{H}_2\text{O}_2$ .	Pt black (catalytic activity between that of colloidal and compact Pt).	Fritzman: <i>Z. anorg. allgem. Chem.</i> , <b>172</b> , 213-233 (1931).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{Fe}$ (bipyridine) $_{2}^{++}$ or $\text{Fe}$ (phenanthroline) $_3$ obtained from $\alpha\alpha'$ -bipyridine or $\alpha$ -phenanthroline.	Limanowski: <i>Roczniki Chem.</i> , <b>12</b> , 782-786 (1932).
Decomposition of $\text{H}_2\text{O}_2$ .	Pt.	Sieverts and Brüning: <i>Z. anorg. allgem. Chem.</i> , <b>204</b> , 291-304 (1932).
Decomposition of $\text{H}_2\text{O}_2$ .	Pt; it is assumed that short-circuit elements of the following type are formed on the surface: $\text{Pt}/\text{adsorbed } p\text{-}p/\text{H}_2\text{O}_2/\text{Pt}$ oxygen with the following electrodic processes: (1) $\text{Adsorbed O} + 2e + \text{H}_2\text{O} + 2\text{OH}'$ (2) $\text{H}_2\text{O}_2 - 2e \rightarrow 2\text{H}' + \text{O}_2$ (3) $2\text{H}' + 2\text{OH}' \rightarrow 2\text{H}_2\text{O}$ the process: $\text{H}_2\text{O}_2 - 2e \rightarrow 2\text{H}' + \text{O}_2$ may occur only at those places of the surface on which $\text{H}_2\text{O}_2$ does not decompose into $\text{H}_2\text{O}$ and $\text{O}$ , i.e., on the inactive places; thus, on the active places adsorbed oxygen is able to act electro-oxidative and on the inactive places $\text{H}_2\text{O}_2$ possesses a reduction potential and in this manner both are engaged in the catalytic process.	Kuhn and Wasserman: <i>Ann.</i> , <b>503</b> , 203-232 (1933).
Decomposition of $\text{H}_2\text{O}_2$ .		Miro and Morales: <i>Soc. espanol. Quim.</i> , <b>31</b> , 103-114 (1933).
Decomposition of $\text{H}_2\text{O}_2$ .		Roiter: <i>Zhur. Fis. Khim.</i> , <b>4</b> , 457-460 (1933).

Table 2 (Continued).

Reaction	Catalyst	Observer
Decomposition of $\text{H}_2\text{O}_2$ .	Charcoal + $\text{MnO}_2$ .	Roiter and Schafran: <i>Ibid.</i> , 4, 461-464 (1933).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{MnO}_2$ , $\text{PbO}_2$ .	Roiter and Gauchman: <i>Ibid.</i> , 4, 465-468 (1933).
Decomposition of $\text{H}_2\text{O}_2$ .	Colloidal Pt (anions of salts $\text{ThCl}_4$ or $\text{Th}(\text{NO}_3)_4$ ) influence the decomposition velocity by forming the Werner complex of hexahydroplatinum acid in place of $\text{OH}^-$ ( $\text{NO}_3^-$ does not show this effect because it enters with difficulty into a complex).	Heath and Walton: <i>J. Phys. Chem.</i> , 37, 977-90 (1933).
Decomposition of $\text{H}_2\text{O}_2$ .	Fe salts (ferrous and ferric).	Haber and Weiss: <i>Proc. Roy. Soc. London (A)</i> , 147, 332-51 (1934).
Decomposition of $\text{H}_2\text{O}_2$ . $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{H}_2\text{O}$ (when $\text{H}_2\text{O}_2$ is added to an acid, iodine solution).	Iodine-iodide system.	Liebhaufsky: <i>J. Am. Chem. Soc.</i> , 56, 2369-72 (1934).
$\text{H}_2\text{O}_2 + \text{I}_2 \rightarrow 2\text{H}^+ + 2\text{I}^- + \text{O}_2$ (oxidation takes place when $\text{H}_2\text{O}_2$ is added to an aqueous iodine solution).		
Decomposition of $\text{H}_2\text{O}_2$ . $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{H}_2\text{O}$ $\text{H}_2\text{O}_2 + \text{Cl}_2 \rightarrow 2\text{H}^+ + 2\text{Cl}^- + \text{O}_2$	Cl acid-chloride system.	Makower: <i>J. Am. Chem. Soc.</i> , 56, 1315 (1934).
Decomposition of $\text{H}_2\text{O}_2$ .	Cholesterin-iodine sols.	Remesow: <i>Ber.</i> , 67, 134-140 (1934).
Decomposition of $\text{H}_2\text{O}_2$ .	Au covered electrolytically with thin layers of Pt, Ir, Rh and Pd black.	Shukow, Glagolewa and Strukowa: <i>Zhur. Obshchei Khimii</i> , 4 (66), 9-12 (1934).
Decomposition of $\text{H}_2\text{O}_2$ .	Sugar charcoal (activated at 1000° and 2 mm. Hg) with $\text{Fe}_2\text{O}_3$ or Pt sols.	Fowler and Walton: <i>Rec. trav. chim.</i> , 54 (4), 476-80 (1935).
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{FeSO}_4 + \text{Na}_2\text{WO}_4$ ; $\text{Na}_2\text{WO}_4$ alone inactive.	Konowalowa: <i>Z. anorg. allgem. Chem.</i> , 222, 81-91 (1935).
Decomposition of $\text{H}_2\text{O}_2$ .	Fe and W salts (simultaneous action of several catalysts).	Konowalowa: <i>Zhur. Fiz. Khimii</i> , 6, 704-14 (1935).
Decomposition of $\text{H}_2\text{O}_2$ .	A mixture of Mn and Cu salts — $\text{CuSO}_4 + \text{MnSO}_4$ ; concentration (0.0015-0.2N) and (0.005-0.15N); small amounts of $\text{Zn}^{++}$ and $\text{Cd}^{++}$ have accelerating action; $\text{Cd}^{++}$ acts more strongly than $\text{Zn}^{++}$ ( $\text{Mn}^{++}$ in a molar or higher conc. does not act catalytically; $\text{Cu}^{++}$ acts only slightly in high conc.).	Bobtelsky, M. and Bobtelsky, L.-Chajkin: <i>Compt. rend.</i> , 201, 604-06 (1935).
Decomposition of $\text{H}_2\text{O}_2$ .	Sugar charcoal made at 400° and activated at 1000° under pressure less than 2 mm. Hg; heating in $\text{N}_2$ atmosphere has no marked influence upon the catalytic activity while $\text{O}_2$ sometimes decreases it considerably; $\text{NaNO}_3$ , $\text{KCl}$ , $\text{BaCl}_2$ do not influence the catalytic properties of sugar charcoal; $\text{Fe}_2\text{O}_3$ and Pt sols inhibit its action; gelatin (0.1% solution) acts in the same way.	Fowler and Walton: <i>Rec. trav. chim.</i> , 54 (4), 476-80 (1935).
Decomposition of $\text{H}_2\text{O}_2$ (in alkaline solution of $\text{H}_2\text{O}_2$ a great number of $\text{HO}_2^-$ anions are formed: $\text{HO}_2^- = \text{HO}_2 + e$ metal (giving off one electron to the metal); when radicals $\text{OH}$ as well as $\text{HO}_2$ are formed, the chain re-	Ag, Pt, Au, Pd and Zn.	Weiss: <i>Trans. Faraday Soc.</i> , 31, 1547-57 (1935).

Table 2 (Continued).

Reaction	Catalyst	Observer
action of catalysis starts to progress; mechanism: decomposition by a transition of an electron from the metal to $H_2O_2$ according to equation: $H_2-O_2 + E \text{ metal} = OH^- + OH$ .		
Decomposition of $H_2O_2$ on active places of amorphous $Fe'''$ hydroxide; by hydrolysis of $Fe'''$ salts the decomposition of $H_2O_2$ is intensive because of formation of basic salts the molecules of which contain OH groups.	Pyridine has slight poisoning action; Fe hydroxides and oxyhydrates (temporary formation of an unstable $Fe'''$ peroxide compound); action decreases from alkali to acid region through $OH^-$ conc.; the activity of H present in orthohydroxide molecule is increased while H ions act oppositely; the aging product (ferric acid from Fe orthohydroxide) is similar to Goethite; when fresh, it is catalytically active.	Krause: <i>Ber.</i> , <b>69</b> , 1982-90, 2708-19 (1936).
Decomposition of $H_2O_2$ . ( $V = R(H_2O_2) \cdot (H^+) (Br^-) (Br^-Br^-)$ .)	Bromine-bromide solution; light of a W lamp (increase of absolute velocity due to the increase in the HBr conc. of the stable state).	Livingston and Schoeld: <i>J. Am. Chem. Soc.</i> , <b>58</b> , 1244-46 (1936).
Decomposition of $H_2O_2$ (with $Cr_2O_7$ an unstable peroxide is formed as an intermediate product).	$Cr_2O_7^{--}$ , $CrO_3$ (the ion $CrO_4^{--}$ does not act catalytically); catalyst additions $Mn^{++}$ , $Cu^{++}$ , $Fe^{+++}$ , $Co^{++}$ and $Ni^{++}$ show a decreasing influence in the sequence given; the smallest concentrations for obtaining a definite catalytic effect are: $Mn^{++}$ 0.00005N $Cu^{++}$ 0.0001N $Co^{++}$ 0.001N $Ni^{++}$ 0.1N concentrations necessary for obtaining the same effect are: $Mn^{++} : Cu^{++} : Co^{++} : Ni^{++} = 1 : 50 : 150 : 7500$ .	Bobtelsky, M. and Bobtelsky, L.-Chajkin: <i>Compt. rend.</i> , <b>203</b> , 1158-60 (1936).
Decomposition of $H_2O_2$ (in neutral and slightly acidified (acetic acid) solutions at 15°).	$Na_2WO_4$ ; among the strongly accelerating cations is $Cu^{++}$ (even below 0.01 mol/l.); action of $Mn^{++}$ , $Co^{++}$ and $Ni^{++}$ is weak even at 0.5 mol/l.; among the anions: $SO_4^{--}$ and $NO_3^-$ are inactive; $I^-$ and $Cl^-$ are strongly active (even in conc. $5-10^{-2}$ N); $F^-$ and $Br^-$ act much weaker (with $F^-$ catalytic effects are obtained only with 0.2-1.0N solutions).	Bobtelsky, M. and Bobtelsky, L.-Chajkin: <i>Compt. rend.</i> , <b>203</b> , 872-74 (1936).
Decomposition of $H_2O_2$ (temp. 30°) (hydration of the catalyst and simultaneous peptizing of the Fe oxyhydrate took place); the colloidal solution acts catalytically; the decomposition is assumed to follow in two steps: (1) $H_2O_2 + Z \rightleftharpoons Z \cdot O + H_2O$ (2) $2Z \cdot O \rightarrow 2Z + O_2$ (Z = catalyzing center)	$Fe_2O_3-Al_2O_3$ (coarse powder); $Al_2O_3$ content: 1%, 2%, 5%, 10% and 20% activity of pure $Al_2O_3$ equal almost zero.	Bloch and Kobosew: <i>Acta Physicochim. U.R.S.S.</i> , <b>5</b> , 417-32 (1936).
Decomposition of $H_2O_2$ in solution (assumed to be a chain reaction obeying exactly Bäckström's law as in photochemical decomposition).	Negative catalytic action show some ketones, methyl alcohol and phenol.	Dain and Epstein: <i>Zhur. Fiz. Khimii</i> , <b>8</b> , 896-903 (1936).
Decomposition of $H_2O_2$ .	Al oxydide hydrosol; addition of anions has decreasing action in this sequence: tartrates > sulfates > acetates > nitrates (the anions are supposed to displace the iodine groups); these have weaker catalytic action than free iodine ions.	Thomas and Cohen: <i>J. Am. Chem. Soc.</i> , <b>59</b> , 268-72 (1937).

Table 2 (Continued).

Reaction	Catalyst	Observer
Decomposition of $\text{H}_2\text{O}_2$ (3% solutions in quartz containers).	Pt (illuminated with x-rays from Coolidge tubes; radiation 30 min.); (first an increase in the activity to a maximum, then a decrease).	Pissarjewsky, Tschrelaschwili and Ssawtschenko: <i>Ada Physicochim. U.R.S.S.</i> , <b>7</b> , 289-94 (1937).
Decomposition of $\text{H}_2\text{O}_2$ (monomolecular reaction); T. 30°.	Colloidal Pt carbonyl (during the catalysis reaction the red sol becomes dark, indicating that colloidal Pt is set free from the carbonyl); the oxygen set free is adsorbed by Pt and exerts a retarding influence upon the reaction catalyzed by pure colloidal Pt.	Sano: <i>Bull. Chem. Soc. Japan</i> , <b>13</b> , 118-126 (1938).
Decomposition of $\text{H}_2\text{O}_2$ in a 4N $(\text{NH}_4)_2\text{SO}_4$ solution.	$\text{Fe}^{+++}$ and citrate <sup>-</sup> ; for citrate <sup>-</sup> / $\text{Fe}^{+++}$ = 0.0.2; the incubation time is up to 3 min.; for citrate <sup>-</sup> / $\text{Fe}^{+++}$ = 0.78, the incubation period increases greatly; the formation of colloidal particles is assumed to be responsible for this phenomenon.	Mordechai, Bobtelsky and Kirson: <i>Compt. rend.</i> , <b>208</b> , 1577-79 (1939).
Decomposition of $\text{H}_2\text{O}_2$ .	Fe salts + Cu salt (1 mol/l. $\text{CuSO}_4$ or $\text{CuCl}_2$ ).	
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{Cr}(\text{CH}_3\text{COO})_3\text{MnSO}_4$ (weak action, sulfates and acetates of Zn); Ni inactive.	
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{Ag}_2\text{O} + \text{Mg}(\text{OH})_2$ or $\text{Cd}(\text{OH})_2$ or $\text{Ni}(\text{OH})_2$ .	
Decomposition of $\text{H}_2\text{O}_2$ .	$\text{K}_2\text{Cr}_2\text{O}_7 + \text{CoCl}_2$ or $\text{K}_2\text{Cr}_2\text{O}_7 + \text{Mn salt}$ .	
Decomposition of $\text{H}_2\text{O}_2$ .	Fe azide ( $\text{FeN}_3$ ).	
Decomposition of $\text{H}_2\text{O}_2$ .	Heavy metal salts in a mixture.	
Decomposition of $\text{H}_2\text{O}_2$ .	Glass wool impregnated with 0.5 g. of 1.54 millimol solution of $\text{CuSO}_4$ .	
Decomposition of $\text{H}_2\text{O}_2$ .	Colloidal Ag.	Wiegel: <i>Z. physik. Chem. (A)</i> , <b>143</b> , 81-93 (1929).

Table 3. Catalytic Decomposition of Nitro-Compounds ( $\text{N}_2\text{O}$ ,  $\text{NH}_2\text{NO}_2$  and  $\text{NaN}_3$ ).

Reaction	Catalyst	Observer
Decomposition of $\text{N}_2\text{O}$ .	$\text{CuO}$ or $\text{CuO} + \text{Al}_2\text{O}_3$ (decrease in the activity of $\text{CuO}$ through $\text{Cr}_2\text{O}_3$ ); the decomposition of $\text{N}_2\text{O}$ is hindered over catalyst $\text{CuO}$ , also by $\text{O}_2$ ; activation heat for $\text{CuO}$ , 26-29 k. cal.; $\text{CuO} + \text{Al}_2\text{O}_3$ , $32 \pm 1$ k. cal. $\text{Al}_2\text{O}_3$ , 29.3 k. cal.; anomalous activation may be interpreted either (1) by increased adsorption capacity (higher adsorption capacity of the spinel, obviously formed in the mixed catalyst) and (2) by increased surface reactivity; the kinetics indicate the probability of the first interpretation.	Georg-Maria Schwab and Staeger: <i>Z. physik. Chem., (B)</i> , <b>25</b> , 418-40 (1934).
Decomposition of $\text{N}_2\text{O}$ .	$\text{CuO}-\text{TiO}_2$ (acts additively); $\text{BeO}$ decreases activity of $\text{CdO}$ and considerably decreases that of $\text{CuO}$ , $\text{CuO}-\text{CdO}$ ; $\text{CuO}-\text{Al}_2\text{O}_3$ ; a promoted mixed catalyst with increased activation heat but with a higher activity than that expected according to the activation rule.	Georg-Maria Schwab and Schultes: <i>Z. physik. Chem., (B)</i> , <b>23</b> , 411-17 (1932).



Table 3 (Continued).

Reaction	Catalyst	Observer
Decomposition of $N_2O$ , $N_2O \rightarrow N_2 + O$ . 5% $O_2$ causes the catalytic reaction to cease; temp. 180–300°; pressure, 10–15 mm. Hg; in the interval 214–280° no temp. dependence is observed; this is explained by assuming that oxygen atoms adsorbed on active places at these temperatures cause a hindrance to active places; the poisoning of the catalyst stops at those temperatures at which the velocity of desorption becomes greater than that of the adsorption.	Bauxite (active surface 5.10 <sup>4</sup> g./cm. about 1/10 of the total surface); active centers assumed to originate through entering of $Fe_2O_3$ into $Al_2O_3$ lattice; the activity of the catalyst disappears when the Fe content is sufficient to build a new lattice.	Sancho: <i>Anales soc. espan. fis. quim.</i> , <b>33</b> , 854–60 (1935).
Decomposition of nitramide in <i>m</i> -cresol; the molecular catalysis constants increase with increase in the acid as well as in the base concentration.		King and Bolinger: <i>J. Am. Chem. Soc.</i> , <b>58</b> , 1533–1542 (1936).
Decomposition of $N_2O$ at 450° temp.; the reaction is slowed down by $O_2$ originating in the reaction by the decomposition and not by added oxygen. $d(N_2O)/dt = K(N_2O)/[1 + b(O_2)]$ $K = 0.383$ $b = 1.10$	Pt or Ag in a "Pyrex" vessel (for method of preparation of the catalyst see Benton and Thacker: (Refer to C. 1934 II 2650).	Steacie and Folkino: <i>Can. J. Research (B)</i> , <b>15</b> , 237–46 (1937).
Decomposition of $N_2O$ to $N_2$ and $O$ ; the amount of $O_2$ and its surface conc. is greater in the presence than in the absence of a catalyst at equal partial pressure; the decomposition in $N_2 + O$ (adsorbed) determines the time factor and the reaction; 20 (adsorbed) $\rightleftharpoons O_2$ (gas) follows rapidly.	NiO.	Wagner and Hauße: <i>Z. Elektroch.</i> , <b>44</b> , 172–78 (1938).
Decomposition of nitramide: $NH_2NO_2 \rightarrow N_2O + H_2O$ mechanism of acid catalysis: $HN=N \begin{smallmatrix} \diagup O \\ \diagdown OH \end{smallmatrix} + H^+ \rightarrow HN + \begin{smallmatrix} OH \\ *N \diagdown \\ OH \end{smallmatrix}$ unstable compound, decomposing into $N_2O$ and oxonium ion.	HCl.	Marlies and La Mer: <i>J. Am. Chem. Soc.</i> , <b>57</b> , 1812–20, 2739 (1935). refer also to Brønsted, Nicholson and Delbanco: (Refer to C. 1934 II 1580).
Decomposition of nitramide at 15–45°.	Anions of trimethyl acetic acid, acetic, benzoic, formic, salicylic, monochloroacetic, dichloroacetic, and <i>o</i> -nitrobenzoic acids.	Baughan and Bell: <i>Proc. Roy. Soc. London (A)</i> , <b>158</b> , 464–78 (1937).
Decomposition of nitramide in aqueous solution; the reaction catalyzed by Pt is between 0 and 1st order; catalysis is interpreted in the sense of a rapid decomposition of nitramide adsorbed by the colloidal particles; the action of poisons, such as iodine, dextrin, glucose and strong acids is explained by selective adsorption hindering the adsorption of nitramide; the nitramide decomposition catalysis with colloidal metals as catalysts is assumed to resemble the corresponding catalysis in the decomposition of $H_2O_2$ .	Colloidal Pt and Au (10 <sup>-4</sup> g. metal per cc. solution); the normal decomposition velocity accelerated 2–10 times; the Pt sol is a more active catalyst than Au sol; by the addition of HCl and $HNO_3$ the catalytic activity of Pt becomes smaller with increasing concentration; this acid influence is ascribed chiefly to the $H^+$ ions, because HCl and $HNO_3$ exert equal effects; influence of salts is on the contrary negligible.	King: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 144–154 (1938).

Table 3 (Continued).

Reaction	Catalyst	Observer
Decomposition of Na azide (NaN <sub>3</sub> ) by I <sub>2</sub> .	Sulfohydryl compounds.	Friedmann: <i>J. prakt. Chem.</i> , <b>146</b> , 179-92 (1936); (Refer to C. 1937 I 275).
A. $\begin{matrix} R-S-H \\ R-S-H \end{matrix} + I_2 \rightarrow$ B. $\begin{matrix} R-SH \\ R-SH \end{matrix} \xrightarrow{I_2} \begin{matrix} R-S \\ R-S \end{matrix} + 2HI$ B. $\begin{matrix} R-SH \\ \downarrow \\ R-SH \end{matrix} \xrightarrow{I_2} + 2NaN_3$ A. $\begin{matrix} R-SH \\ R-SH \end{matrix} + NaI + 3N_2$		
$A + I_2 \rightarrow B \rightarrow C + 2HI$ $\downarrow$ $B + 2NaN_3$ $A + 2NI + 3N_2$ , etc.		

Table 4. Catalytic Decomposition of Various Inorganic Compounds.

Reaction	Catalyst	Observer
Decomposition of Ag oxalate.	Ag <sub>2</sub> S (germs) (induction period shortened); dispersion degree important	Sheppard and Vanselow: <i>Kodak Res. Lab. Abs. Bull.</i> , <b>15</b> , 89; <i>J. Am. Chem. Soc.</i> , <b>52</b> , 3468-70 (1931/1932).
Decomposition of acid Ca carbonate [Ca(HCO <sub>3</sub> ) <sub>2</sub> ] in aqueous solution.	CaCO <sub>3</sub> , coke, active coal, graphite, fiber alumina; less active are Fe, Al—Cu splinters.	Stumper: <i>Chimie &amp; industrie</i> , <b>32</b> , 1023-37 (1934); (Refer to C. 1932 II 1742, 3048, 3049).
Decomposition of carbonate in a closed receiver, first into CO <sub>2</sub> and then into CO; industrial production of CO.	Fe—C alloy or carbon in the form of charcoal as well as coke heated to a red glow.	Mauclert: F.P. 753,658, Oct. 21, 1933.
Decomposition of COSe (carbonyl selenide) at 120° temp., also at 130 and 140°.	Allotropic Se surfaces (preparation method by Pearson and Robinson): (Refer to C. 1932 II 34); black and red Se have different catalytic action; Se $\beta$ or Se'' has a higher catalytic activity than Se, Se $\alpha$ or Se $\gamma$ ; if the reaction vessel is made of SiO <sub>2</sub> instead of porcelain, the yield is increased 4 times (the catalytic activity of porcelain for the reaction: 2CO $\rightarrow$ CO <sub>2</sub> + C is eliminated).	Purcell and Zahoorbux: <i>J. Chem. Soc.</i> , 1937, 1029-35.
Decomposition of hypochlorites.	CoSO <sub>4</sub> (anodic inertness of Co silicide in mineral acids is ascribed to the formation of a surface oxide film); CoSO <sub>4</sub> in conc. H <sub>2</sub> SO <sub>4</sub> stable (CoSO <sub>4</sub> decomposed at 800° in CoO, SO <sub>2</sub> and O <sub>2</sub> ); CoSO <sub>4</sub> in electrolysis forms Co <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> which with hot water liberates O <sub>2</sub> ; with HCl solution, Cl <sub>2</sub> , and with organic acids, CO <sub>2</sub> .	Fink: <i>Trans. Electroch. Soc.</i> , <b>71</b> , Preprint (6 pp.) (1937).
Decomposition of Na and K formate to oxalate; T. 240°; 85% of K formate converted.	2-4% NaNH <sub>2</sub> ; NaNH <sub>2</sub> almost as active as the alkali metals, but not so dangerous in application; ThO <sub>2</sub> accelerates selectively the carbonate formation; Cu powder in a small amount causes chiefly oxalate formation, while an increase in the catalyst amount shifts the reaction toward carbonate formation; decomposition with formation of CO <sub>2</sub> and C precipitation does not take place even for an excess of Cu.	Freidlin: <i>Zhur. Priklad. Khim.</i> , <b>11</b> , 975-80 (1938).

## PART V

## Catalytic Decomposition in Organic Chemistry

Table 1. Catalytic Decomposition of Carbon Monoxide.

Reaction	Catalyst	Observer
Decomposition of CO. $2\text{CO} \rightarrow \text{C} + \text{CO}_2$	Reduced Ni.	Bahr and Bahr: <i>Ber.</i> , <b>61</b> , 2177-2183 (1928). Doriba and Ri: <i>Bull. Chem. Soc. Japan</i> , <b>3</b> , 18-25 (1929)
Decomposition of CO.	Fe, Ni, Co or their oxides.	Fischer and Tropsch: <i>G. P.</i> (1930).
Decomposition of CO.	$\text{Fe}_3\text{C}$ , $\text{Fe}_2\text{O}_3$ , Fe.	Tutija: <i>Sci. Papers Inst. Phys. Chem. Research (Tokyo)</i> , <b>10</b> , 69-82, (1929). Tutija: <i>Bull. Inst. Phys. Chem. Research (Tokyo)</i> , <b>2</b> , 76 (1929). Watanabe: <i>Ibid.</i> , <b>2</b> , 37, 38 (1929). Watanabe: <i>F.P.</i> 721,961, June 27, 1932.
Decomposition of CO.	$\text{Ni}_3\text{C}$ ( $\text{Ni}_4\text{C}$ ) (formed from NiO at 284°; decomposes into $\text{Ni}_3\text{C}$ and C); $\text{Ni}_3\text{C}$ quite stable at 285°; free Ni found in early stages, then changes entirely into carbides.	Tutija: <i>Ibid.</i> , <b>3</b> , 951-973 (1931).
Decomposition of CO.	Mo carbide.	Tutija: <i>Sci. Papers Inst. Phys. Chem. Research (Tokyo)</i> , <b>19</b> , 120-121 (1932).
Decomposition of CO.	A mixture of Fe and C (practically free from S compounds).	General Carbo-Naphtha. Co.: <i>F.P.</i> 729,461, July 25, 1932.
Decomposition of CO (under pressure at low or moderate temp.).	Solid catalysts consisting of one metal of the Fe group (Fe, Ni, or Co) in mixture with oxides or hydroxides of Mn, V, Cr, U, Zn, Al, Cd or Cu, also silicates, chromates, molybdates or tungstates.	I. G. Farbenindustrie A.-G. (Schmidt): <i>U.S.P.</i> 1,894,126, Jan. 10, 1933.
Decomposition of CO or gases containing it to soot; T. 350-650° (regulated temp. velocity, enrichment in $\text{CO}_2$ amount and addition, all factors kept uniform during C precipitation).	Fe oxide.	Löf: <i>N.P.</i> 57,313, November 16, 1936.
Decomposition of CO. $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$ T. greater than 184°; C precipitated on the catalyst attacked by $\text{H}_2$ may be removed as $\text{CH}_4$ .	ZnO.	Burwell and Taylor: <i>J. Am. Chem. Soc.</i> , <b>59</b> , 697-699 (1937).
Decomposition of CO. $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$ 50% $\text{CO} + 50\%$ $\text{CO}_2$ (initial mixture is circulated under diminished pressure); T. 300-500°.	Fe, FeO, $\text{Fe}_2\text{O}_3$ ; catalyst obtained by reduction at 300-500° from Fe glance to spongy Fe is very active; (loses its activity in the presence of $\text{H}_2$ or CO when heated to 900°).	Tschufarow and Kulikow: <i>Metal-lurg.</i> , <b>12</b> , No. 3, 3-7 (1937).

Table 2. Catalytic Decomposition of Methane.

Reaction	Catalyst	Observer
Decomposition of $\text{CH}_4$ . $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$	Coke, Fe, Co, Ni on porcelain or kaolin.	Nauss: <i>G.P.</i> 226,609 (1909).
Decomposition of $\text{CH}_4$ .	Fe, Co, Ni, Cu on $\text{MgO}$ , $\text{Al}_2\text{O}_3$ .	Badische Anilin und Soda Fabrik: <i>Russ. P.</i> 24,386 (1911). <i>Hung. P.</i> 58,719 (1911).
Decomposition of $\text{CH}_4$ .	Melted Mg, Ni (melted Ag, Cu).	Gerard: <i>U.S.P.</i> 1,418,385 (1920).
Decomposition of $\text{CH}_4$ .	Ni, Cr, Cu (in powder form).	Hopkinson: <i>U.S.P.</i> 1,497,751 (1923).
Decomposition of $\text{CH}_4$ .	Coke; $\text{UO}_2$ or its alkaline solution.	Battig: <i>E.P.</i> 271,491 (1927). Lidow and Kusnetzow: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>33</b> , 940 (1905).

Table 2 (Continued).

Reaction	Catalyst	Observer
Decomposition of $\text{CH}_4$ .	Fireproof nets.	Battig: B.P. 271,483 (1927).
Decomposition of $\text{CH}_4$ .	Ni.	Jamaguti: <i>Bull. Chem. Soc. Japan</i> , <b>2</b> , 289-294 (1927).
Decomposition of $\text{CH}_4$ .	Glowing metal wire.	Schwab and Pietsch: <i>Z. physik. Chem.</i> , <b>126</b> , 473 (1930).
Decomposition of $\text{CH}_4$ .	Fe, Co, Ni oxides + Ni vanadate or Co uranate or Fe tungstate (T. greater than $800^\circ$ ).	N. V. de Bataafsche Petroleum Maatschappij: G.P. 29,816, May 15, 1933.
Decomposition of $\text{CH}_4$ .	$\text{ZnO} + \text{CuO}$ (Cu-rich preparation causes "structural promotion" preventing the sintering effect at high temp.; Zn-rich preparations cause "synergetic promotion").	Kostelitz and Hüttig: <i>Kolloid-Z.</i> , <b>67</b> , 265-277 (1934).
Decomposition of $\text{CH}_4$ .	Zr ore, active charcoal, slate ash, Hg. kaolin (best action), electrical discharge ( $1050^\circ$ ), V or Mo, Ni on kieselguhr.	Klukwin and Klukwina: <i>Khim. Tverdogo Topliva</i> , <b>6</b> , 130-146 (1935).
Decomposition of methane; T. 900-1300°; pressure 1-20 mm.; reaction velocity is expressed by the equation: $dx/dt = K(a-x)^n$ where $n$ is greater than 1 and depends on the heterogeneity of the contact surface.	Electrically heated Pt wire.	Kubokaw: <i>Rev. phys. Chem. (Japan)</i> , <b>11</b> , 82-96 (1937).
Decomposition of $\text{CH}_4$ .	Mixture of corundum, kaolin, $\text{NiO}$ , $\text{Al}(\text{OH})_3$ and $\text{MgCO}_3$ (as carrier are used two substances with greatly different melting or softening points which are above the working temp. of the catalyst; the substances are mixed with the catalyst, molded, dried, and burned at a temp. above the working temp. of the catalyst).	Bamag-Meguín A.-G.: F.P. 841,479, May 22, 1939.

Table 3. Catalytic Decomposition of Ethane.

Reaction	Catalyst	Observer
Decomposition of ethane; T. $635^\circ$ ; increase of pressure from 1 to 26 atm. decreases the dehydrogenation reaction: $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ and increases the reaction: $2\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_4 + \text{C}_2\text{H}_2$ .		Dintzes, Zharkova, Zherko and Frost: <i>Zhur. Obshchei Khim.</i> , <b>7</b> , 1063 (1937).
Decomposition of ethane; proceeds according to the mechanism expressed in the following equations: $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ $\text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \text{CH}_2$ $\text{CH}_2 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_4$ (rapid) $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 \rightarrow \text{C}_4\text{H}_{10} \rightarrow \text{CH}_4 + \text{C}_2\text{H}_6$ $\quad \quad \quad \uparrow$ $\quad \quad \quad \text{H}_2 + \text{C}_2\text{H}_4$ $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_6$		Storch and Kassel: <i>J. Am. Chem. Soc.</i> , <b>59</b> , 1240 (1937).
Decomposition of ethane by steam starts at $430^\circ$ ; $\text{C}_2\text{H}_6 \rightleftharpoons 2\text{CH}_4$ and is completed at $500$ - $550^\circ$ ; without a catalyst the decomposition starts at $500^\circ$ and reaches a maximum at $700^\circ$ .	Silica gel impregnated with Ni.	Cryder and Porter: <i>Ind. Eng. Chem.</i> , <b>29</b> , 667 (1937).
Decomposition of ethane; the process involves three stages: (1) $\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$ ; (2) the formation of an unstable intermediate compound and (3) decomposition of the latter and formation of the final products such as $\text{CH}_4$ and condensation products.		Travers: <i>Trans. Faraday Soc.</i> , <b>33</b> , 735 (1937).

Table 3 (Continued).

Reaction	Catalyst	Observer
Decomposition of hydrocarbons; if the assumption that the process amounts to a break in C—C bonds holds true, the yield of individual products corresponds to the Boltzmann distribution law postulating that all the carbon atoms are united by bonds of the same strength; as this is not the case, <i>e.g.</i> , when first a splitting of a C—H bond takes place with formation of molecular hydrogen and an olefin, in which the double bond is usually located at the end of the chain, and then the double bond exerts an influence upon the remaining C—C bonds in the molecule; so it happens that the adjacent single bond is strengthened, while the next one is weakened. Schmidt thinks such a readjustment of the strength of C—C bonds takes place to a smaller extent throughout the whole molecule and therefore determines the location of the cracking of the molecule; this generalization has been found applicable to phenylated aliphatic compds. in which the double bond of the aromatic portion of the molecule weakens the C—C bond once removed from the ring.		Schmidt: <i>Z. physik. Chem.</i> (A), <b>159</b> , 337 (1932).

Table 4. Catalytic Decomposition of Acetaldehyde.

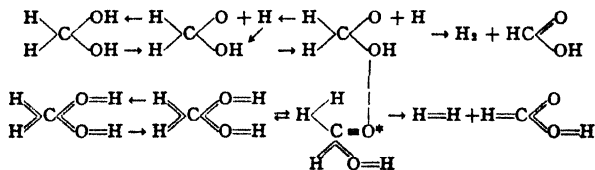
Reaction	Catalyst	Observer
Decomposition of acetaldehyde.	Hg compounds: HgO, HgSO <sub>4</sub> , Hg <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> in H <sub>3</sub> PO <sub>4</sub> .	Boiteau: P.P. 474,826 (1913). Canadian Electrical Products: U.S.P. 1,578,454 (1926).
Decomposition of ethylidene diacetate. $\text{CH}_3\text{CH}(\text{OCOCH}_3)_2 \rightarrow \text{CH}_3\text{CHO} + (\text{CH}_3\text{CO})_2\text{O}$	Zn, ZnCl <sub>2</sub> .	Société Chimie des Usines du Rhône: G.P. 284,996 (1914). G.P. 322,746 (1917). G.P. 451,533 (1924).
Decomposition of acetaldehyde.	Zn.	Bayer Co.: G.P. 360,325 (1919).
Decomposition of acetaldehyde.	Strong acids on carriers.	Konsortium für Elektrochemische Industrie: G.P. 391,674 (1921).
Decomposition of acetaldehyde (gaseous).	Metals.	Allen and Hinshelwood: <i>Proc. Roy. Soc. London</i> (A), <b>121</b> , 141-155 (1928).
Decomposition of acetaldehyde (by heat).	I <sub>2</sub> , Br <sub>2</sub> , HCl, H <sub>2</sub> S (catalytically active substances have high polarization) (NH <sub>3</sub> , pyridine, HCN and SO <sub>2</sub> catalytically inactive) (substances that react with the aldehyde at low temp. are catalytically inactive).	Fromherz: <i>Z. physik. Chem.</i> (B), <b>25</b> , 301-318 (1934).
Decomposition of acetaldehyde.	I <sub>2</sub> (in all reactions catalyzed with iodine, a hydrogen atom is displaced and a bond broken).	Hinshelwood, Clusius and Hadman: <i>Proc. Roy. Soc. London</i> (A), <b>128</b> , 88-92 (1930); (Refer to C. 1930 II 2865).
Decomposition of acetaldehyde; T. 480°; (the amount of acetaldehyde decomposed by O <sub>2</sub> is the greater the larger the excess of acetaldehyde).	NO (walls of the reaction vessel covered with carbon which accelerates the reaction); balls of SiO <sub>2</sub> in the reaction vessel decrease the reaction velocity; (surfaces of walls which are clean as well as those covered with carbon, no influence).	Verhock: <i>Trans. Faraday Soc.</i> , <b>31</b> , 1533-1536 (1935); <b>31</b> , 1527-1533 (1935).
Decomposition of acetaldehyde to CO and CH <sub>4</sub> ; T. 175°; atmospheric pressure.	Ni (prepared by precipitation from Ni nitrate with excess of NaOH and joint reduction at 400° (Cu, Fe, Co may be used)).	Ebert: <i>J. Phys. Chem.</i> , <b>39</b> , 421-424 (1935).

Table 4 (Continued).

Reaction	Catalyst	Observer
Decomposition of acetaldehyde.	Small amounts of ether.	Fletcher and Rollefson: <i>J. Am. Chem. Soc.</i> , <b>58</b> , 2129-2135 (1936).
Decomposition of acetaldehyde; T. 320-350°; 100-170 mm. pressure. $\text{CH}_3\text{CHO} + \text{Br}_2 \rightarrow \text{CH}_3\text{Br} + \text{HBr} + \text{CO}$ a volatile Br compound originates which is heavier than $\text{CH}_3\text{Br}$ and $\text{HBr}$ .	Br (10-30 mm. Hg).	Brenschede and Schumacher: <i>Ber.</i> , <b>70</b> , 452-456 (1937).
Decomposition of acetaldehyde: $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$ ; CO is led over the catalyst and $\text{Ni}(\text{CO})_4$ formed; after the action of CO and a decrease in the activity of the catalyst (up to 50%), the surface of the catalyst becomes inhomogeneous; the active places are first attacked by CO; the greatest decrease in activity corresponds to the smallest amount of Ni led off, which indicates that the number of active particles on the catalyst may be very small; the activation energy calculated from experimental data does not undergo essential changes through the action of CO; therefore no dependence exists in the present case between the activation energy and the activity of the catalyst.	Ni on $\text{Al}_2\text{O}_3$ (1 : 1).	Chwatow: <i>Zhur. Obshchei Khim.</i> , <b>9</b> , 819-24 (1939).

Table 5. Catalytic Decomposition of Formaldehyde.

Reaction	Catalyst	Observer
Decomposition of $\text{HCHO}$ . $2\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_6$	Al alcoholate.	Konsortium für Elektrochemische Industrie: G.P. 277,111 (1912).
Decomposition of $\text{HCHO}$ .	Rh black (metals of the Pt group act much weaker than Rh).	Tschugajew: <i>Ann. inst. plaine (U.S.S.R.)</i> , <b>7</b> , 210 (1929).
Decomposition of $\text{HCHO}$ ; very little CO formed over Os; much CO formed over Rh, Ru, Pd.	Os and Ru, Pd, Ir.	Müller, E. and Müller, F.: <i>Z. Elektroch.</i> , <b>27</b> , 558 (1921); <b>31</b> , 41-45 (1925).



\* Note: The dotted line designates the place of attack in the catalyst

Table 6. Catalytic Decomposition of Propionic Aldehyde.

Reaction	Catalyst	Observer
Thermal decomposition of gaseous propionic aldehyde.	Pt surface.	Stearie and Morton: <i>Can. J. Research</i> , <b>4</b> , 582-590 (1931).
Decomposition of propionic aldehyde $\text{C}_2\text{H}_5\text{CHO} \rightarrow \text{C}_2\text{H}_6 + \text{CO}$ ; it is concluded that in all reactions catalyzed with iodine, a hydrogen atom is displaced and a bond is broken.	I <sub>2</sub> .	Bairstow and Hinshelwood: <i>Proc. Roy. Soc. London (A)</i> , <b>142</b> , 77-88 (1933).

Table 7. Catalytic Decomposition of Ketones.

Reaction	Catalyst	Observer
Decomposition of ketones under high pressure.	Fe tube.	Ipatieff and Petrov: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>50</b> , 93 (1927); <i>Ber.</i> , <b>60</b> , 1956 (1927); <i>Chem. Abs.</i> , <b>22</b> , 217 (1928).
Thermal decomposition of cyclic ketones (homo-isophoron and 1-methylcyclohexanone; pulegon to phenol and cymol. T. 196-220°.		Ipatieff and Petrov: <i>Ber.</i> , <b>60</b> , 2545 (1927); <i>Chem. Abs.</i> , <b>22</b> , 1135 (1928).
Decomposition of ketones with the formation of ethyl ester (ethyl aceto-acetate or aceto-acetic ester).	Normal alkali sulfates act upon alkali bisulfates.	Goodhue and Dunlap: <i>J. Am. Chem. Soc.</i> , <b>50</b> , 1916 (1928).
Decomposition of the hydrazo compound of ethyl ketone; 11 mm. pressure; final products: methyl dipicrate and methyl ethyl indole.	ZnCl <sub>2</sub> .	Arbuzov and Kotermel: <i>Zhur. Obshchei Khim.</i> , <b>2</b> , 397 (1932).
Decomposition of nitroso- $\beta$ -alkyl amino ketones; a new method of preparing diazomethane; diazotization in the aliphatic series, open chain; no derivatives obtained from addition products of primary amines with mesityl oxide, Me <sub>2</sub> C(NRNO)CH <sub>3</sub> ; undergo catalytic decomposition with alkali and give a diazo solution from which azo-benzene and also $\beta$ -naphthol are prepared by coupling.	Alkali.	Jones and Renner: <i>J. Chem. Soc.</i> , <b>1933</b> , 363.
Thermal decomposition of acetone to methane and ketene.	Monomolecular reaction; chain reaction	Allen: <i>J. Am. Chem. Soc.</i> , <b>58</b> , 1052 (1936). Winkler and Hinshlewood: <i>Proc. Roy. Soc. London (A)</i> , <b>149</b> , 340 (1935); (Refer to C. 1936 I 1600). Rice and Herzfeld: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 284 (1934); (Refer to C. 1934 II 587).

Table 8. Catalytic Decomposition of Ethyl Alcohol.

Reaction	Catalyst	Observer
Decomposition of ethyl alcohol with H <sub>2</sub> SO <sub>4</sub> to ethylene.	Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , MgO, KOH, K <sub>2</sub> SO <sub>4</sub> , C	Bondt, Deiman, van Trosswyk and Lauwerenburg: (1795); refer to Passagex: <i>Bull. soc. chim.</i> (5), <b>2</b> , 1000 (1902) (1935).
Decomposition of ethyl alcohol.	Glowed kaolin.	Dayman: (1795).
Decomposition of alcohols: (1) aldehydic and ketonic; (2) olefinic (no aldehyde decomposition).	Zn and brass. WO <sub>3</sub> and UO <sub>3</sub> .	Ipatieff: "Catalytic Reactions at High Pressures and Temperatures," New York, The Macmillan Company, 1936.
Decomposition of ethyl alcohol.	Heated Al <sub>2</sub> O <sub>3</sub> or clay.	Huff: <i>Trans. Am. Electrochem. Soc.</i> , <b>36</b> , 167-186 (1920).
Decomposition of ethyl alcohol.	ZnO.	Adkins and Lazier: <i>J. Am. Chem. Soc.</i> , <b>48</b> , 1647-1677 (1926).
Decomposition of ethyl alcohol.	P <sub>2</sub> O <sub>5</sub> .	Balarew: <i>Z. anorg. allgem. Chem.</i> , <b>148</b> , 105-110 (1926).
Decomposition of ethyl alcohol.	TiO <sub>2</sub> .	Rudisill and Engelder: <i>J. Phys. Chem.</i> , <b>30</b> , 106-113 (1926).
Decomposition of ethyl alcohol.	Oxides of Al, Sc, Ga.	Georg-Maria Schwab: <i>Z. physik. Chem. (B)</i> , <b>12</b> , 5406 (1929).
Decomposition of ethyl alcohol.	Hydroxides of alkalis: KCH <sub>3</sub> NH <sub>2</sub> greater than KC <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> greater than KCH <sub>2</sub> NH <sub>2</sub> greater than KNH <sub>2</sub> ; alkali halides.	Walker, Russel and Marschker: <i>J. Phys. Chem.</i> , <b>34</b> , 2554 (1930).
Decomposition of ethyl alcohol.	Ni on pumice.	Walker, Russel and Marschker: <i>J. Phys. Chem.</i> , <b>34</b> , 2554 (1930).

Table 8 (Continued).

Reaction	Catalyst	Observer
Decomposition of ethyl alcohol.		Backhaus: U.S.P. 1,376,665, May 3, 1921.
Decomposition of ethyl alcohol.		Ipatieff: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>35</b> , 449 (1903). Ipatieff: <i>J. prakt. Chem.</i> , <b>67</b> , 420 (1903). Ipatieff: <i>Ber.</i> , <b>37</b> , 2961 (1904).
Decomposition of ethyl alcohol.	NiCrO <sub>4</sub> .	Boomer and Morris: <i>Can. J. Research</i> , <b>6</b> , 471-484 (1932).
Decomposition of ethyl alcohol; T. 240-500°; CH <sub>4</sub> may be formed by (1) decomposition of CH <sub>3</sub> CHO; (2) hydrogenation of CO(CO <sub>2</sub> ); (3) decomposition of C <sub>2</sub> H <sub>4</sub> ; H <sub>2</sub> O and CO <sub>2</sub> may be added.	Mixed catalysts.	Boomer and Morris: <i>Can. J. Research</i> , <b>10</b> , 743-58 (1934).
Decomposition of ethyl alcohol according to Lebedew's method (commercial divinyl preparation) to <i>o</i> -cresol, traces of <i>p</i> -cresol and methyl ethyl phenol; the mixture of crude phenols may be condensed with HCHO and urotropin to iditol, a plastic mixture for lacquers.		Lichosherstow, Petrov and Alexejew: <i>Zhur. Obshchei Khim.</i> , <b>4</b> , (66), 1274-1278 (1934). Lebedew: <i>Ibid.</i> , <b>3</b> , 698 (1933).
Decomposition of ethyl alcohol; T. 250°; the course of catalytic decomposition is not influenced by the water content of the contact.	Alumina; optimum activity found at 5.5% by weight H <sub>2</sub> O in the catalyst (activity of the catalyst decreases strongly in the case of most active contacts); in case of water-free alumina, no decrease in activity is observed.	Munro and Horn: <i>Can. J. Research</i> , <b>12</b> , 707-10 (1935).
Decomposition of ethyl alcohol to ethyl acetate without addition of acid; normal pressure; T. 220-450°; conversion 6-12 cc. alcohol/hr. over 5 g. contact; optimum temperature 350°; yield, 24%.	0.1-0.2% thorium oxide containing CuO.	Iwannikow and Gawrilowa: <i>Zhur. Khim. Prom.</i> , <b>12</b> , 1256-1260 (1935).

Table 9. Catalytic Decomposition of Methyl Alcohol.

Reaction	Catalyst	Observer
Decomposition of CH <sub>3</sub> OH. CH <sub>3</sub> OH → COH <sub>2</sub> + H <sub>2</sub> .	Pt.	Hofmann: <i>Ann.</i> , <b>145</b> , 357 (1868).
Decomposition of CH <sub>3</sub> OH. 2CH <sub>3</sub> OH → (CH <sub>3</sub> ) <sub>2</sub> O + H <sub>2</sub> O.	Al <sub>2</sub> O <sub>3</sub> .	Delco Light Co. (Bichowsky): E.P. 278,353 (1927). F.P. 641,580 (1927).
Decomposition of CH <sub>3</sub> OH. CH <sub>3</sub> OH → COH <sub>2</sub> + H <sub>2</sub> .	Pt.	Delco Light Co. (Bichowsky): F.P. 677,973 (1928).
Decomposition of CH <sub>3</sub> OH.	Cu or Zn.	Frolich, Fenske and Quiggle: <i>Ind. Eng. Chem.</i> , <b>20</b> , 694-698 (1929).
Decomposition of CH <sub>3</sub> OH.	Zn-Cu or Cr <sub>2</sub> O <sub>3</sub> .	Fenske and Frolich: <i>Ind. Eng. Chem.</i> , <b>21</b> , 1052 (1929).
Decomposition of CH <sub>3</sub> OH.	Zn or Cr.	Plotnikow and Iwanow: <i>Zhur. Khim. Prom.</i> , <b>6</b> , 940-943 (1929).
Decomposition of CH <sub>3</sub> OH.	Zn + Cr <sub>2</sub> O <sub>3</sub> .	Huffman and Dodge: <i>Ind. Eng. Chem.</i> , <b>21</b> , 1056-1061 (1929).
Decomposition of CH <sub>3</sub> OH. CH <sub>3</sub> OH → COH <sub>2</sub> + H <sub>2</sub> .	ZnO.	Dohse: <i>Z. physik. Chem. (B)</i> , <b>8</b> , 159 (1930).
Decomposition of CH <sub>3</sub> OH.	Cu.	Plotnikow and Kaganowa: <i>Zhur. Khim. Prom.</i> , <b>7</b> , 672 (1930).
Decomposition of CH <sub>3</sub> OH.	Ni aerosol.	Gibbs and Liander: <i>Trans. Faraday Soc. (Part II)</i> , <b>26</b> , 656-662 (1930).



Table 9 (Continued).

Reaction	Catalyst	Observer
Decomposition of $\text{CH}_3\text{OH}$ .	$\text{CuO} + \text{ZnO}$ (reduced at $190-300^\circ$ ).	Nussbaum and Frolich: <i>Ind. Eng. Chem.</i> , <b>23</b> , 1386-1389 (1931).
Decomposition of $\text{C}_2\text{H}_5\text{OH}$ .	Surfaces of Mn compounds.	Williamson and Taylor: <i>J. Am. Chem. Soc.</i> , <b>53</b> , 327 (1931).
Decomposition of $\text{CH}_3\text{OH}$ .	Zn oxalate.	Rosenkranz: <i>Z. physik. Chem. (B)</i> , <b>14</b> , 401-412 (1931). Rosenkranz: <i>Chimie &amp; industrie</i> , <b>29</b> , No. 6, 785 (1933).
Decomposition of $\text{CH}_3\text{OH}$ .	Metals of the Pt group.	Huttig and Weissberger: <i>Festschrift</i> , <b>157</b> (9) (Siebert) 193, 198 (1931).
Decomposition of $\text{CH}_3\text{OH}$ .	$\text{ZnO}$ with different particle size.	Huttig, Kostelitz and Feher: <i>Z. anorg. allgem. Chem.</i> , <b>198</b> , 206-218 (1931).
Decomposition of $\text{CH}_3\text{OH}$ .	$\text{ZnO}$ (catalytic activity decreases with high pressure used in compressing the preparation).	Kostelitz and Huttig: <i>Z. Elektroch.</i> , <b>39</b> , 362-368 (1933).
Decomposition of $\text{CH}_3\text{OH}$ .	$\text{Cr}_2\text{O}_3$ .	Huttig and Strial: <i>Z. Elektroch.</i> , <b>39</b> , 368-373 (1933).
Decomposition of $\text{CH}_3\text{OH}$ .	Solid or liquid Zn (activity decreases by melting the catalyst at $420^\circ$ ).	Steacie and Elkin: <i>Proc. Roy. Soc. London (A)</i> , <b>142</b> , 437-465 (1933).
Decomposition of $\text{CH}_3\text{OH}$ T. $220^\circ$ .	$\text{Cu} + \text{Zn}$ .	Solotow and Schapiro: <i>Zhur. Obshchei Khim.</i> <b>4</b> (66), 679-682 (1934).
Decomposition of $\text{CH}_3\text{OH}$ .	37 parts by weight (15.5%) $\text{Cu} + 15$ parts by weight (48.0%) $\text{Ni}$ (both prepared from $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) melted together and 50 parts by weight fibrous pieces added (mesh size, $10 \times 8$ ).	Carbide and Carbon Chemicals Corporation (Eversole): U.S.P. 2,010,427, Aug. 6, 1935.
Decomposition of $\text{CH}_3\text{OH}$ ; T. $300-375^\circ$ , 100% decomposition T. $300-325^\circ$ , 100% decomposition T. $400^\circ$ .	$\text{ZnS} + 5\%$ $\text{CdS}$ , or $\text{MoS}_2$ , or $\text{CuS}$ . $\text{ZnS} + 1\%$ $\text{CdS}$ , or $\text{MoS}_2$ , or $\text{Sb}_2\text{S}_3$ , $\text{ZnO}$ .	Dolgow, Karpinski and Ssilina: <i>Khim. Tverdogo Topliva</i> , <b>5</b> , 470-474 (1935).
Decomposition of $\text{CH}_3\text{OH}$ . (1) to formaldehyde to $\text{CO}$ and $\text{H}_2$ . (2) to dimethyl ether to $\text{CH}_4$ and $\text{CH}_2\text{O}$ . (a) $\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}_2$ . (b) $2\text{CH}_3\text{OH} \rightarrow (\text{CH}_3)_2\text{O} + \text{H}_2\text{O}$ . Temp. at which decomposition starts:	(a) Ag wool, Fe. (b) Al.	Kuss: <i>Angew. Chem.</i> , <b>49</b> , 483-486, (1936).
Quartz	650°	
Glass	400°	
Ag	500°	
Pt	300°	
Al	450°	
Fe	550°	
CaO	450°	
Coal	450°	
Decomposition of alcohols; T. $320^\circ$ .	$\text{Al}_2\text{O}_3$ gel (dried in streaming $\text{N}_2$ , air or $\text{H}_2$ , $\text{C}_2\text{H}_4$ for different intervals of time at $150-300^\circ$ ) the oxide prepared in $\text{N}_2$ stream contained the smallest amount of water and the oxide prepared in $\text{C}_2\text{H}_4$ the largest amount of water; with decreasing water content the amount of ethylene formed in the reaction increases and that of $\text{H}_2$ decreases.	Spinoglio: <i>Atti mem. accad. sci. Padova</i> (5), <b>51</b> , 25-35 (1935).
Decomposition of $\text{CH}_3\text{OH}$ to aldehyde by condensation of which are formed complex esters which further decompose with liberation of $\text{CO}_2$ ; the decomposition of paraldehyde opposite to the monomer aldehyde follows with formation of $\text{H}_2$ and $\text{CO}_2$ .	$\text{CeO}_2$ (reduced during the reaction to $\text{Ce}_2\text{O}_3$ ) (action of both oxides the same) (alcohol is dehydrogenated by the action of $\text{Ce}_2\text{O}_3$ ); $\text{CrO}_3$ does not act as a hydrogenating catalyst.	Anissimow: <i>Zhur. Obshchei Khim.</i> <b>7</b> (69), 1931-1934 (1937).

Table 9 (Continued).

Reaction	Catalyst	Observer
Decomposition of methanol to formaldehyde (the formaldehyde decomposes further and very small yields obtained;) more favorable results obtained with Re partially poisoned with $As_2O_3$ as well as with $H_2S$ ; it is assumed that Re catalyst poisoned with $H_2S$ contains $ReS_2$ ; yield, 41.7% (for $H_2S$ poisoned Re catalyst); yield, 30.2% (for $As_2O_3$ poisoned Re catalyst); T. 400°.	Finely divided Re.	Platonow, Tomilow and Tur: <i>Ibid.</i> , 7, (69), 1803-1804 (1937).

Table 10. Catalytic Decomposition of Higher Alcohols.

Reaction	Catalyst	Observer
Decomposition of isopropyl alcohol.	Alkali salt solution.	Akerlof: <i>J. Am. Chem. Soc.</i> , <b>48</b> , 3046-3063 (1926).
Decomposition of isopropyl alcohol.	Bauxite.	Dohse: <i>Z. physik. Chem. (B)</i> , <b>6</b> , 343-354 (1930). Dohse and Kälberer: <i>Ibid.</i> , <b>5</b> , 131-155 (1928).
Decomposition of higher alcohols.	Kaolin.	Skärblom: <i>Svensk Kem. Tid.</i> , <b>40</b> , 119-125 (1929).
Decomposition of higher alcohols.	Alkali halides.	French: <i>J. Am. Chem. Soc.</i> , <b>51</b> , 3215-3225 (1929).
Decomposition of higher alcohols.	$KCH_3NH_2$ greater than $KC_2H_5NH_2$ greater than $KCH_3NH$ greater than $KNH_3$ .	Miller and Kilpatrick: <i>Ibid.</i> , <b>53</b> , 3217 (1931).
Decomposition of higher alcohols.	$Al_2O_3$ , ZnO.	Adkins and Folkners: <i>Ibid.</i> , <b>53</b> , 1420-1424 (1931).
Decomposition of higher alcohols.	Surfaces of Mn compounds.	
Decomposition of propyl alcohol.	Chromium oxide gel (prepared in an air stream; showed an increase in the amount of propylene and a decrease in $H_2$ , with decreasing content of water in the catalyst).	Spinoglio: <i>Atti mem. accad. sci. Padova (5)</i> , <b>51</b> , 25-35 (1935).

Table 11. Catalytic Decomposition of Acetic Acid.

Reaction	Catalyst	Observer
Decomposition of acetic acid to acetone.	$BaCO_3$ .	Squibb: <i>J. Am. Chem. Soc.</i> , <b>17</b> , 187 (1895).
Decomposition of acetic acid. $2CH_3COOH \rightarrow CH_3CO \cdot CH_3 + CO_2 + H_2O$	$Al_2O_3$ , $ThO_2$ , $UO_2$ , Cu.	Senderens: <i>Bull. soc. chim. (4)</i> , <b>3</b> , 824 (1908); ( ) <b>5</b> , 905, 916 (1909). Sabatier and Senderens: <i>Ann. chim. (8)</i> , <b>4</b> , 476 (1905).
Decomposition of acetic acid. $2CH_3COOH \rightarrow CH_3CO \cdot CH_3 + CO_2 + H_2O$	Cu, $MnO_2$ .	Société de Acières et Forge de Firminy: Swiss P. 88,187 (1919).
Decomposition of acetic acid to acetone.	$Ca(OH)_2 + MgO$ .	Canadian Electrical Products Co., Ltd.: Swed. P. 92,107 (1919).
Decomposition of acetic acid.	CaO ( $BaO$ ) and their acetates.	Stockholm Superfosfat Fabriks: B.P. 171,391 (1921).
Decomposition of acetic anhydride. $2CH_3CO_2H \rightarrow (CH_3CO)_2O + H_2O$	Phosphates of elements of the 2nd and 3rd group. Alkali phosphate (melt).	Konsortium für Elektrochemische Industrie: G.P. 410,363 (1922). G.P. 411,106 (1922). Konsortium für Elektrochemische Industrie: G.P. 417,731 (1921). E.P. 230,063 (1925).
Decomposition of acetic acid to acetone.	Charcoal.	Kultaschew: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>55</b> , 383 (1924).
Decomposition of acetic acid.	Strong acids and bases.	Elear and Oländer: <i>Z. anorg. allgem. Chem.</i> , <b>147</b> , 295-311 (1925).

Table 11 (Continued).

Reaction	Catalyst	Observer
Decomposition of phenyl acetic acid.	H <sub>2</sub> SO <sub>4</sub> .	Dittmar: <i>J. Phys. Chem.</i> , <b>33</b> , 553-556 (1929).
Decomposition of acetic acid to acetone; yield 90-95%; the old non-catalytic method consisted in dry distillation of acetic powder.	Compounds of Th; coke; oxides of alkali earths, Mn also oxides of U, Th, Zn, Cr.	E.P. 315,818 (1929). Kultaschew: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>55</b> , 383 (1924).
Decomposition of acetic acid to acetone; T. 320-450°; yield, 90-95%.	Compounds of Th, Mn, also UO <sub>2</sub> , ThO <sub>2</sub> , ZnO, Cr <sub>2</sub> O <sub>3</sub> .	B.P. 315,818 (1929).
Decomposition of acetic acid (in vapor state) to acetone; yield 92%; T. 400°; unconverted acetic acid less than 0.4%.	Carbon containing Cu, Al, V, 2A steel, ceramic masses.	Deutsche Gold- und Silber Scheideanstalt (Roessler, Walter and Schultze); G.P. 581,047, Kl 12a, July 20, 1933.
Decomposition of acetic acid vapor to acetic acid anhydride T. 400-850°; preheated at 350-450°.	Metals bound to phosphoric acid; about 10% NaCl and 10% KCl, also K and Ba tetrametaphosphate.	Dreyfus: E.P. 390,845, May 11, 1933. F.P. 745,322, May 9, 1933.
Decomposition of acetic acid by first passing its vapors at high temperature through purifying adsorbents which in themselves do not decompose the acid so that no adsorption takes place; the previous purification increases the yield of the ketone and decreases the loss in the activity of the catalyst.	Oxides of Th, U, Cr, etc.; adsorbents, coke or charcoal.	F.P. 791,160 (1935).

Table 12. Catalytic Decomposition of Formic Acid.

Reaction	Catalyst	Observer
Decomposition of formic acid to H <sub>2</sub> and CO <sub>2</sub> in the cold.	Rhodium or iridium black.	St. Claire-Deville and Debray: <i>Compt. rend.</i> , <b>78</b> , 1782 (1874).
Decomposition of aqueous solutions of formic acid.	Ir, Pt, Rh, Pd decrease the velocity at the beginning; Os and Ru increase the velocity to a maximum after an induction period and then decrease it; the decrease is not due to decrease in the conc. but to the fact that the high degree of dispersion of freshly precipitated metals rapidly decreases; in general, metals of the Pt group can produce decomposition because, when they are finely divided they are able to adsorb both H atoms of formic acid.	Muller and Leopatel: <i>Monatsh.</i> , <b>53</b> , 54, 825 (1929).
Decomposition of gaseous formic acid.	Cu—Au mixed crystals; Cu : Au = 3 : 1, 1 : 1 and 1 : 3; activation heat 24.0-24.5 k. cal; activation energy is independent of the size of the crystals; Cu <sub>3</sub> Au alloy or other alloys, activation heat 24.0 k. cal; Cu <sub>3</sub> Au catalytic activity different; activation heat 21.0 and 24.5 k. cal. independent of the size of the crystals.	Rienacker: <i>Z. Elektroch.</i> , <b>40</b> , 487-488 (1934).
Decomposition of formic acid to H <sub>2</sub> O and CO; formation of CO only.	Conc. H <sub>2</sub> SO <sub>4</sub> . H <sub>2</sub> SeO <sub>4</sub> HCOOH : H <sub>2</sub> SeO <sub>4</sub> = 100 : 1 HCOOH : H <sub>2</sub> SeO <sub>4</sub> 6% CO <sub>2</sub> 1 : 1 >50% CO <sub>2</sub> 1 : 5 (H <sub>2</sub> SeO <sub>4</sub> reduced thereby to Se) HCOOH : H <sub>2</sub> SeO <sub>4</sub> 10 : 1 2 : 1 (CO <sub>2</sub> found only at the end of the reaction).	Dolique: <i>Bull. soc. chim.</i> (5), <b>2</b> , 1489-1491 (1935). Oechsner de Coninck and Chouvenet: <i>Bull. acad. roy. Belg.</i> , 1905, 601-3; <i>Ann. chim. anal. chim. appl.</i> , <b>21</b> , 114 (1916).

Table 12 (Continued).

Reaction	Catalyst	Observer
Decomposition of formic acid in the vapor phase to $H_2 + CO_2$ .	Cu—Pd alloy; Cu—Au alloy; in case of oriented atom distribution the activation energy is decreased by 6–10 k. cal. (the change in catalytic activity is not related directly to the change in the lattice type, but is connected by the observers with electronic binding (an increased catalytic action results from increase of diamagnetism, magnetic superstructure effect, etc.).	Rienacker, Wessing and Trautmann: <i>Z. anorg. allgem. Chem.</i> , <b>236</b> , 252–262 (1938).

Table 13. Catalytic Decomposition of Organic Acids.

Reaction	Catalyst	Observer
Decomposition of propionic acid to diethyl ketone; T. 590° T. 530°	Zn. $CaCO_3$ .	Ipatieff and Shuman: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>36</b> , 764 (1904).
Decomposition of oxalic acid with hot conc. $H_2SO_4$ .	0.05% $H_2O$ ; 1% $H_2SO_3$ causes a violent reaction.	Bredig and Fraenkel: <i>Ber.</i> , <b>39</b> , 1756 (1906).
Decomposition of organic acids; the yield of the ketone decreases with an increase in the molecular weight of the acid.	Al, Th, Cr oxides; catalyst alumina in case of decomposition of acetic anhydride instead of acetic acid has a short life due to excessive carbonization.	Senderens: <i>Bull. soc. chim.</i> (4), <b>3</b> , 827 (1908).
Decomposition of organic acids: (1) phthalic acid or phthalic anhydride to benzoic acid and $CO_2$ . (2) phthalic acid or phthalic anhydride to benzene and $CO_2$ .	$Na_2CO_3$ , $CaCO_3$ , etc., in the presence of water vapor. $CuSO_4$ . $CdO + Al_2O_3$ in the presence of water vapor.	I. G. Farbenindustrie A.-G.: G.P. 445,565 (1925). Dupont: U.S.P. 1,712,753 (1924). I. G. Farbenindustrie A.-G.: B.P. 262,101 (1926).
Decomposition of fatty acids to $H_2$ and $CO_2$ .  CO and $H_2O$ formed exclusively.  HCHO and $CH_3OH$ formed.	Pt, Ir, Rh and Pd. Os and Ru (reduced Cu). Broken Jena glass. White glass. ZnO. $TiO_2$ .  Th. Cu—Au mixed crystals (ratio 1 : 1 or 1 : 3). Ferrous oxide, lime. Blue oxide of tungsten.	
Decomposition of oleic acid.	$UO_2$ , alumina, silica, Zr.	Marks and Howard, Jr.: <i>J. Phys. Chem.</i> , <b>32</b> , 1040–1048 (1927).
Decomposition of stearic acid.	Sulfurized naphthenes—similar to Petrow's contact mass.	Kister: <i>Zhur. Khim. Prom.</i> , <b>5</b> , 1176–1178 (1928).
Thermal decomposition of fatty acids vapors to avoid local superheating by melted or liquid fuels; acetic anhydride is prepared; separation of water combined with thermal decomposition, e.g., acetic acid heated with 1 to 2 parts by volume $CH_4$ in the presence of sodium metaphosphate at 600–650° and led over finely dispersed Ni at 700–750°.	Rb, Te, or other metals and alloys containing decomposition catalysts Ni or Co.	Dreyfus: F.P. 737,610, Dec. 14, 1932. F.P. 737,611, Dec. 14, 1932.

Table 14. Catalytic Decomposition of Esters.

Reaction	Catalyst	Observer
Preparation of acetic acid anhydride by cracking ethylidene diacetate: $CH_3 \cdot CH(O \cdot COCH_3)_2 \rightarrow CH_3CHO + (CH_3 \cdot CO)_2O$	Zn.  $ZnCl_2$ .  Strong acids on carriers.	Born Elektrizitätswerke A.-G.: G.P. 284,996 (1914). The Bayer Company: G.P. 360,325 (1919). Société Chimie des Usines du Rhône: G.P. 451,533 (1924). Konsortium für Elektro-chemische Industrie: G.P. 391,674 (1921).

Table 14 (Continued).

Reaction	Catalyst	Observer
Ketonic decomposition of the ethyl ester of acetic acid.		Goodhue and Dunlap: <i>J. Am. Chem. Soc.</i> , <b>50</b> , 1916-1922 (1928).
Decomposition of esters.	ZnCl <sub>2</sub> anhydrous.	Underwood and Basil: <i>Ibid.</i> , <b>52</b> , 395-397 (1930).
Decomposition of ortho esters.	Al oxide.	Sigmund and Hershdonfer: <i>Monatsh.</i> , <b>58</b> , 280-288 (1931).
Decomposition of acids and esters.	ZnCl <sub>2</sub> anhydrous.	Underwood and Basil: <i>J. Am. Chem. Soc.</i> , <b>53</b> , 2200-2202 (1931).
Decomposition of acetyl acetate.	Al <sub>2</sub> O <sub>3</sub> .	Bancroft: <i>J. Phys. Chem.</i> , <b>35</b> , 2943-2949 (1931).
Decomposition of esters.	Ni	Pearce and Wing: <i>Ibid.</i> , <b>36</b> , 703-712 (1932).
Decomposition of esters.		Pearce and Ott: <i>Ibid.</i> , <b>31</b> , 102-114 (1927).
Decomposition of esters of aliphatic acids in the gaseous phase; H <sub>2</sub> SO <sub>4</sub> diluted with 2H <sub>2</sub> O; reaction same as in the liquid phase but occurs at a higher temperature and more slowly due to the greater proportion of H <sub>2</sub> SO <sub>4</sub> effective in the liquid phase; at 110° EtCO <sub>2</sub> Pr gives propylene and the equivalent amount of EtCO <sub>2</sub> H; at 210°, EtCO <sub>2</sub> H is also decomposed.	H <sub>2</sub> SO <sub>4</sub> on pumice.	Senderens: <i>Compt. rend.</i> , <b>196</b> , 979-982 (1933).
Decomposition of ethyl aceto-acetic ester to dehydroaceto acetic acid: $2\text{CH}_3\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5 \rightarrow \text{C}_6\text{H}_4\text{O}_4(1 \cdot \text{R}=\text{CH}_2) + 2\text{C}_2\text{H}_5\text{OH}.$ It is believed that the reaction proceeds in two steps: (1) re-esterification between enol- and keto- aceto-acetic ester with establishment of an equilibrium; (2) a one-sided Claisen condensation.	Catalyzed by small amounts of alkali present in the glass of the container.	Arndt and Nachtwey: <i>Ber.</i> , <b>57</b> , 1489 (1924). Arndt, Eistert, Scholz and Aron: <i>Ber.</i> , <b>69</b> , 2373-2380 (1936).
Decomposition of diazoacetic ester; T. 0-35°; the velocity is three times greater in D <sub>2</sub> O, and the velocity increase is explained by a smaller zero point energy of the reacting complex in D <sub>2</sub> O which causes a decrease in activation energy: 800 ± 150 cal.	Protons and deuterons.	Gross, Steiner and Krauss: <i>Trans. Faraday Soc.</i> , <b>34</b> , 351-356 (1938).
Decomposition of esters of glyceric phosphoric acid; the K salt of diphenylphosphoric acid and hexose diphosphoric acid, as well as the alkali and Ca salts of inositol hexa-phosphoric acid show a weaker splitting.	Lanthanum hydroxide gel (optimum splitting ability lies in the weak alkali region pu = 7.5-8.0).	Bamann and Meisenheimer: <i>Ber.</i> , <b>71</b> , 1711-1720 (1938).
Decomposition of esters of glyceric phosphoric acid.	Metal hydroxide gels; hydroxides of Bi, Cu and Sb are completely inactive; hydroxides of Zr and Th catalyze splitting; Ti(OH) <sub>3</sub> no influence; Pb hydroxide little active; Mn hydroxide activates; hydroxide of La very active; Y very little action; hydroxides of the Al group completely inactive.	Bamann and Meisenheimer: <i>Ber.</i> , <b>71</b> , 1980-1983 (1938).
Conversion of meta- into ortho-phosphate; with respect to ester splitting, the hydroxides show selective behavior.	Hydroxides of rare earths very active, especially those of La, Ce, Pr, Nd, Sa, Y, Zr, and Th.	Bamann and Meisenheimer: <i>Ber.</i> , <b>71</b> , 2086-2089 (1938).

Table 14 (Continued).

Reaction	Catalyst	Observer
Decomposition of triphosphoric and pyrophosphoric acids, as well as their esters.	Metal hydroxides (La, Ce, Zr, and Rh) show good action; moderate influence have Pb and Mn; weak action of Al and Zn.	Bamann and Meisenheimer: <i>Ber.</i> , 71, 2233-36 (1938).

Table 15. Catalytic Decomposition of Ethers.

Reaction	Catalyst	Observer
Thermal decomposition of ethyl ether.	Pt.	Steacie and Campbell: <i>Proc. Roy. Soc. London (A)</i> , 128, 451-458 (1930).
Decomposition of ethyl ether at 700-1000°; $(C_2H_5)_2O \rightarrow 2CH_4 + 1/2C_2H_4 + CO$ Action of catalyst supposedly consists of a condensation of active molecules.	Pt and W.	Taylor and Schwartz: <i>J. Phys. Chem.</i> , 35, 1044-1053 (1931).
Decomposition of ethyl ether; increases 20 times with $Cl_2$ and 6 times with $I_2$ .	$I_2$ and $Cl_2$ .	Bairstow: <i>Trans. Faraday Soc.</i> , 29, 1227 and 1228 (1933).
Decomposition of $CH_3COC_2H_5(CH_3)_2N$ .	$I_2$ and $Cl_2$ ; catalytic influence insignificant.	
Decomposition of gaseous ethers: (a) dimethyl ether. (b) methyl ethyl ether; T. 400-550°.	$I_2$ ; no catalytic influence. $I_2$ ; activation heat, 38,000 cal.	Alfred and Clusius: <i>J. Chem. Soc.</i> , 1930, 2607-2615.
(1) $CH_3O \cdot C_2H_5 \rightarrow CH_4 + CH_3 \cdot CHO$ (2) $CH_3 \cdot CHO \rightarrow CH_4 + CO$ (c) methyl isopropyl ether; T. 450-520°.	Activation of the reacting molecule depends on the structure of a total molecule and not on the presence of a definite group; simultaneous reactions; total activation heat, 29,500 cal.	
(1) $CH_3OCH(CH_3)_2 \rightarrow CH_4 + CO(CH_3)_2$ (2) $CH_3O \cdot CH(CH_3)_2 \rightarrow CH_4O + C_2H_4 \rightarrow CO + H_2 + C_2H_4$		
(d) methyl- <i>tert</i> -butyl ether decomposes with difficulty.	Strong effect.	
Decomposition of benzyl ethers of aromatic oxy- or mercapto-compounds or their substitution products; benzyl groups split off free phenols and thiophenols obtained; benzene ethers treated with reducing agents excluding $H_2$ in the presence of catalysts.	Reducing agents: $SnCl_2$ , Sn, or Zn in the presence of acids.	I. G. Farbenindustrie A.-G.: E.P. 375,253, July 21, 1932.

Table 16. Catalytic Decomposition of Organo-Metallic Compounds.

Reaction	Catalyst	Observer
Decomposition of hydrocarbons with $H_2O$ vapor, $CO_2$ , $O_2$ , or air in $H_2$ -CO or $H_2$ -CO-N <sub>2</sub> mixtures, or thermal decomposition in C and $H_2$ .	Metals of the Fe group with unburned artificial or natural aluminum silicate, especially kaolin; catalyst contains in addition oxides of alkaline earths including MgO.	I. G. Farbenindustrie A.-G. (Wietzel and Heunicke): G.P. 554,551, Kl 12i, July 11, 1932.
Decomposition of organo-metallic compounds: $P(C_6H_5)_4$ under $H_2$ pressure with formation of benzene: (1) $Pb(C_6H_5)_4 + 2H_2 \rightarrow Pb + 4C_6H_6$ $Sn(C_6H_5)_4$ under $H_2$ pressure with formation of diphenyl: (2) $Sn(C_6H_5)_4 + 2H_2 \rightarrow Sn + 2C_6H_5 \cdot C_6H_5$ $Pb(C_6H_5)_4$ and $Sn(C_6H_5)_4$ (in the presence of alcohol).	$Pd > Au > Ag > Ni$ (without $H_2$ pressure) for $Pb(C_6H_5)_4$ ; $Pd > Ni > Ag > Au$ (with $H_2$ pressure) for $Sn(C_6H_5)_4$ ; $Pd > Ag > Au > Ni$ (without $H_2$ pressure), and $Pd > Ni > Ag > Au > Cu$ (with $H_2$ pressure); reaction (1) is catalyzed chiefly through Ni; addition of Pd catalyzes reaction (2); without $H_2$ pressure the decomposition occurs according to scheme (1). $Pd > Au > Ag > Ni$ in the case of $Pb(C_6H_5)_4$ ; $Pd > Ag > Ni > Au$ in the case of $Sn(C_6H_5)_4$ .	Koton: <i>Ber.</i> , 66, 1213-1215 (1933).

Table 16 (Continued).

Reaction	Catalyst	Observer
Decomposition of organo-metallic compounds: diphenyl Hg at 200-250°:	Diphenyl Hg: Pd > Pt > Ag > Au > Co > Cu > Fe > Ni.	Rasuwaew and Koton: <i>Ber.</i> , <b>66</b> , 854-858 (1933).
(1) $R_2Hg \rightarrow R \cdot R + Hg$ , and dibenzyl Hg at 25-75° under $H_2$ pressure (decomposing almost by melting):	Dibenzyl Hg: Pd > Pt > Ag > Au > Cu > Ni > Fe > Co, most active catalysts (Pd and Pt) cause decomposition at normal temperature; activity series of metals under $H_2$ pressure:	Rasuwaew and Koton: <i>Zhur. Obshchei Khim.</i> , <b>3</b> (65), 792-797 (1933).
(2) $R_2Hg + H_2 \rightarrow 2RH + Hg$ , decomposition of phenyl Hg in absence of catalyst follows (2); Ni, Fe and Co are directed almost exclusively to (2); Pd to (1); triphenyl Pb in the presence of $H_2$ gives diphenyl-Ni only in sufficient amount of $H_2$ ; when using a large amount of Ni decomposition proceeds with the formation of benzene.	Diphenyl Hg: Pd > Pt > Ni > Ag > Au > Co > Cu > Fe. Dibenzyl Hg: Pd > Pt > Ni > Au > Ag > Fe > Co > Cu.	
Thermal decomposition of Pb tetraphenyl, $Pb(C_6H_5)_4$ , giving quantitatively diphenyl in the absence of $H_2$ at 252°; in addition, benzene and p-diphenyl benzene are formed at higher temperatures.	Ni.	Dull and Simons: <i>J. Am. Chem. Soc.</i> , <b>55</b> , 4328 (1933).
Decomposition of organo-metallic compounds: $\alpha-C_6H_4H_2 < CH_3C_6H_4 < BrC_6H_4$ $C_6H_5OC_6H_4 < CH_3OC_6H_4 < C_6H_5$ $C_6H_5CH_2$	Pd. Pd > Ni > Au > Ag > Cu (in case of alcohol), and Pd > Au > Ag > Ni > Cu (in case of tetralene).	Rasuwaew and Koton: <i>Ber.</i> , <b>66</b> , 1210-1213 (1933). Rasuwaew and Koton: <i>Zhur. Obshchei Khim.</i> , <b>4</b> (66), 647-652 (1934).
This result is not in agreement with that of Kharash; by decomposition, the corresponding diphenyl derivatives, except the di- and $\alpha$ -naphthyl in which naphthalene is formed due to the presence of a second $\alpha$ -naphthyl radical which is dehydrated; decomposition of diphenyl Hg compounds in alcohol or tetralene follows according to the series written above; formation of derivatives of the type KR or the hydrogenation of the radical RH may take place; in alcohol, the latter reaction occurs only with $\alpha$ -naphthyl Hg; in other cases, diphenyl derivatives are formed; in case of tetralene, on the other hand, the formation of the theoretical amount of benzene is observed.		
Decomposition of organo-metallic compounds: $Pb(C_6H_5)_4$ and $Sn(C_6H_5)_4$ ; under $H_2$ pressure, benzene is obtained; without $H_2$ pressure and in alcohol, diphenyl is formed.	Pd, Ni, Au, Ag, Cu.	Koton: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>4</b> (66), 653-657 (1934).

Table 17. Catalytic Decomposition of Halogenated Organic Compounds.

Reaction	Catalyst	Observer
Decomposition of an aliphatic monobromine derivative: $C_nH_{2n+1}Br \rightarrow HBr + C_nH_{2n}$	$ThO_2$ , $Al_2O_3$ , kaolin; $Al_2O_3$ and $Ca_3P_2O_8$ not influenced by $H_2$ halide.	Senderens: <i>Compt. rend.</i> , <b>200</b> , 2137-2149 (1935).
Decomposition of isobutyl bromide; T. 260° $(CH_3)_2C=CH_2 + HBr \rightarrow (CH_3)_2CBrCH_3$ (in cold, recombines with HBr faster than with HCl); n-butyl bromide decomposed over $ThO_2$ and $Al_2O_3$ ; T. 280-300°; HBr fumes; propyl bromide (propene + HBr); T. 250 and 270° over $Al_2O_3$ ; T. 235 and 255° over $ThO_2$ ; T. 260-280° over kaolin;	$ThO_2$ .	





Table 18 (Continued).

Reaction	Catalyst	Observer
Decomposition of benzene under $H_2$ pressure; yield of diphenyl is smaller than in experiments without $H_2$ ; small amounts of $CH_4$ and $C_2H_4$ formed; from toluene, with and without a catalyst, originate chiefly benzene and complex unknown liquid hydrocarbons; xylene gives with like treatment toluene and complex liquid and solid hydrocarbons; from decomposition of squalene ( $C_{30}H_{50}$ ), under $H_2$ pressure, aliphatic hydrocarbons and higher terpene compounds are obtained.	$Al_2O_3$ , no catalytic influence.	Oda: <i>Sci. Papers Inst. Phys. Chem. Research (Tokyo)</i> , <b>17</b> , 32-56 (1931).
Decomposition (decarboxylation) of phthalic anhydride.	Decomposition catalyst associated with a permutogenetic material.	Jaeger: <i>U.S.P.</i> 1,892,766, March 1, 1932.
Decomposition of CO to form alkali-soluble ingredients.	Fe.	Bahr: <i>Ges. Abhandl. Kennlinis Kohle</i> , <b>10</b> , 160-163 (1932).
Decomposition of heavy hydrocarbon oils into light hydrocarbon oils.	Alloys of Sn and Fe remain solid by the reaction temperature (cause decomposition of $H_2O$ with formation of $H_2$ ); Ni, Cr, or Co may be added.	Forwood: <i>Can. P.</i> 338,106, Dec. 26, 1933.
Decomposition of hydrocarbon oils, brown coal generator tar containing 20% boiling at $300^\circ$ gives a product containing 50% boiling at $300^\circ$ at 5 atm. pressure in the presence of 5% metallic Ti heated at $400^\circ$ .	Fe or not highly alloyed steels over which a carbon precipitation occurs by decomposition; Ti, Zr, Th, or the elements B or Si, as well as their alloys, may be used.	I. G. Farbenindustrie A.-G.: <i>G.P.</i> 578,504, Kl 23b, June 15, 1933.
Decomposition of saffrol and isosaffrol; T. $190^\circ$ and $198^\circ$ ; the course of decomposition 1,2-dihydrosaffrol; 3,4(HO) $_2$ - $C_6H_4$ Pr; $p$ -HOC $_6H_4$ Pr, or $p$ -MeC $_6H_4$ OH.	Active charcoal.	Kimura: <i>J. Chem. Soc. Japan</i> , <b>54</b> , 14-21 (1933).
Decomposition of gaseous hydrocarbons at $600$ - $800^\circ$ led through a heated liquid bath of molten alkali or alkaline-earth halides, depending upon starting material and temp. conditions; low-boiling hydrocarbons or olefins are obtained; work may be carried out at optional pressures.	Si; silicates of Mg or Al; oxides of Mo or Cr; mixtures of silicates and Si or difficultly reducible oxides: Ca, Ba, Sr, Mg or rare earths, also aluminates, tungstates, vanadates, chromates, or uranates of the alkalies or alkaline earths; $SiO_2$ , C, S, carbides, or metallic catalysts.	Dreyfus: <i>E.P.</i> 386,169, Feb. 16, 1933.
Decomposition of xylene to 7% benzene and 11% toluene; m-xylene shows greatest resistance to decomposition; best-suited fraction, $C_8H_8 \cdot C_8H_8$ .	2% $AlCl_3$ .	Popow: <i>Azerbaidzhanskoe Neftyanoe Khoz.</i> , <b>14</b> , No. 7/8, 21-24 (1934).
Decomposition of paraffinic hydrocarbons; the yield of $CH_4$ was improved by adding gas (50% $H_2$ +50% CO); 302 l./kg. oil and 217 l./kg. unsaturated hydrocarbon oil instead of 260 l./kg. oil without the addition of washing gas.	Uranium oxide and its alkaline solution.	Bunte and Lang: <i>Gas-u-Wasser-Jach</i> , <b>78</b> , 98-101, Feb. 9, 1935.
Decomposition of hexane, cyclohexane and light benzene (low-boiling hydrocarbons).	Mo with definite conc. of Si added produces best action; this conc. coincident with the value for the smallest activity in high-pressure hydrogenation.	Griffith and Plant: <i>Proc. Roy. Soc. London (A)</i> , <b>148</b> , 191-194 (1935).
Decomposition of $C_{11}H_{18}O_4$ dissolved in a solution of absolute ether and sodium ethylate with $H_2SO_4$ to form benzoyl hydroperoxide, $C_6H_5CO(O \cdot OH)$ ; no catalytic influence on $C_{11}H_{18}O_4$ in the presence of $MnO_2$ powder (acts normally in the decomposition of $H_2O_2$ ).	Pt and $MnO_2$ ; $MnO_2$ obtained from $KMnO_4$ ; $MnO_2$ also shows catalytic action in the case of the peroxide, while fine black powder, Kahlbaum, may not contain the lower Mn oxides in the $MnO_2$ used, which therefore may account for the different behavior toward the benzoyl peroxide and benzoyl hydroperoxide.	Beresowskaja and Ssermichatowa: <i>Zhur. Fiz. Khim.</i> , <b>6</b> , 114-124 (1935).

Table 18 (Continued).

Reaction	Catalyst	Observer
Decomposition of $\text{CHCl}_3$ ; T. $512^\circ$ ; initial pressure more than 50 mm. (reaction of the first order).	$\text{I}_2$ and nitrogen oxide.	Verhock: <i>Trans. Faraday Soc.</i> , 31, 1521-1526 (1935).
Decomposition of chloral; T. $400^\circ$ ; activation energy, 37,100 cal./g. molecule.	$\text{NO}$ ; small amounts of $\text{O}_2$ have no influence, but large amounts of $\text{O}_2$ accelerate reaction.	
Thermal decomposition of propane to 10% by volume higher olefins; T. $790$ - $810^\circ$ 28% $\text{C}_2\text{H}_4$ , 15% $\text{H}_2$ , 6% $\text{CH}_4$ homologs and 41% $\text{CH}_4$ .	Steel containers containing more than 20% Cr and 0.4 Si and less than 0.2% Ni.	I. G. Farbenindustrie A.-G.: E.P. 469,101, Aug. 19, 1937. Ital. P. 346,169, Oct. 17, 1936.
Decomposition of butane to 25% higher olefins; 13% $\text{C}_2\text{H}_4$ , 10% $\text{H}_2$ , 37% $\text{CH}_4$ and 15% $\text{CH}_4$ homologs; no carbon precipitation takes place.		
Decomposition of olefin- $\text{SO}_2$ complexes, for example, propylene and $\text{SO}_2$ ; T. $0^\circ$ ; 2-butene- $\text{SO}_2$ complex; T. $80^\circ$ ; moderate splitting; high polymerization products obtained from $\text{SO}_2$ ; unsaturated hydrocarbons are split to low molecular S- and O-containing organic compounds.	5% NaOH 20% NaOH alkali or alkaline earths, hydroxides, $\text{NH}_4\text{OH}$ , liquid $\text{NH}_3$ , amines, substituted amino-compounds.	Phillips Petroleum Co. (Snow): U.S.P. 2,102,654, Dec. 21, 1937.
Decomposition of methyl acetate or methyl propionate to ketene or methyl ketene; T. $500$ - $1000^\circ$ ; under diminished pressure (28-180 mm.).	Na metaphosphate or silica gel impregnated with $\text{H}_3\text{PO}_4$ , dehydrated or hydrated boron oxide.	Dupont: E.P. 504,626, May 25, 1939.

Table 19. Catalytic Cracking Processes.

Reaction	Catalyst	Observer
Cracking processes.	$\text{AlCl}_3$ .	Gulf Refining Company (McDuffie and McAfee): U.S.P. 1,478,444 (1913). Gulf Refining Company: G.P. 394,443 (1914). Gulf Refining Company (Alexander): U.S.P. 1,381,098 (1916). Gulf Refining Company (McAfee): <i>Chem. Met. Eng.</i> , 36, 422 (1929) Naphtali: "Light Hydrocarbon Oils," Berlin, 1928.
Cracking processes.	Metallic melts: Sn, Bi.	Barbet: F. P. 399,722 (1908). Melamid: F. P. 539,715 (1921). E.P. 221,559 (1923). U.S.P. 1,602,310 (1923). Blumner: G.P. 340,991, Kl 12r, Gr 1, Oct. 19, 1920. Tropsch: <i>Brennstoff-Chem.</i> , 5, 100 (1924). Frey and Faber: <i>Chem. Ztg.</i> , 46, 379 (1922).
Cracking processes.	Melts and alloys of metals.	Fresh: U.S.P. 1,212,620 (1915). Danckwardt: U.S.P. 1,141,529 (1914). U.S.P. 1,594,666 (1924). Jansen: G.P. 456,312 (1927). E.P. 278,235 (1927). U.S.P. 1,672,459 (1925). Clancy: U.S.P. 1,658,116 (1922). U.S.P. 1,721,728 (1926).

Table 19 (Continued).

Reaction	Catalyst	Observer
Gyro-process; (low-pressure vapor-phase cracking process for any grade of petroleum oil, producing a motor fuel of high anti-knock rating); the striking feature of the Gyro process is the limited coke formation permitting a long operation period.	$\text{Fe}_2\text{O}_3$ .	Gyro-Process Corporation (Ram- age); U.S.P. 1,687,890 (1925). Gyro-Process Corporation (Weaver); U.S.P. 1,708,247 (1925).
Cracking processes; (conversion of high-boiling organic compounds, such as mineral oils and tars to low-boiling organic compounds by use of catalysts).	Cracking catalysts: $\text{AlCl}_3$ , melts of metals, alloys and salts; active charcoal.	
Cracking of heavy fractions of pitch generator tar followed by oxidation of ethylene to formaldehyde;		Deschalit: <i>Ukrain. Khem. Zhur.</i> , 11, 348-353 (1936).
(1) fraction b.p. 280-360° cracked over T. 600-700°; catalytic cracking (6%) up to 180° yields more of the light fractions than without a catalyst (2%); the amount and composition of gases is little different with and without the catalyst;	Silica gel.	
(2) catalytic oxidation of ethylene formed to formaldehyde; T. 440-450°.	Vanadium.	
Cracking of a peat generator tar fraction (b.p. 280-360°) containing 22.4% phenols, 11.5% paraffins, 3.2% pyridine cmpds., and 2.6% carboxylic acids; T. 600-700°; yield: low-boiling fractions and a gas of high calorific value containing: 15-36% $\text{CH}_4$ , 20-44% $\text{H}_2$ , 16-21% $\text{C}_2\text{H}_4$ , 15-17% propene, and about 1% of each of the following: $\text{CO}_2$ , $\text{O}_2$ , $\text{CO}$ , $\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_4$ .	Silica gel.	Deschalit: <i>Ukrain. Khem. Zhur.</i> , 11, 348 (1936).
Decomposition of a phenol-free Gdov shale tar; T. 200-300° yield, 24-25% of a product containing 6-7% of benzene and toluene, as well as gases more rich in unsaturates than those obtained in cracking petroleum.	Cr-Ni steel retort.	Kozhewnikow: <i>Novosti Tekhniki</i> 34, 30 (1936).
Cracking of shale oil directly yields gasoline of 65 octane number (plant operated in France since 1936).		Berthelot: <i>Rev. pétrolière</i> , 757, 1515 (1937).
Cracking of heavy shale oil in (1) liquid phase to form a stable oil without destroying the paraffin wax; at the cracking temp. held a few minutes under pressure the crude shale oil passed through the catalyst gave a high-boiling oil and a higher-melting wax (small loss of the original paraffin wax); (2) vapor-phase cracking of light neutral oil from coal tar yields a colorless stable distillate.	(1) Molten lead. (2) Pt wire.	Rishi and Heda: <i>J. Soc. Chem. Ind. Japan</i> , 40, (1937).
Cracking of (evaporated) mineral oils in vapor phase; T. 400-538°; the oil vapors are led with such high velocity through the catalysts that these are maintained in a steadily rotating motion.	Ton, oxides of Al, Mg, Si, or sulfides of metals of the 6th group of the periodic system; these however are advantageously applied together with oxides of Ca, Mg, Al, Si; catalyst is used in the form of grains (the used catalysts are regenerated with air; these likewise are led through with such velocity that the catalyst remains steadily in motion).	Standard Oil Development Co.: F.P. 829,582, June 30, 1938.

Table 19 (Continued).

Reaction	Catalyst	Observer
Cracking of gas oil ( $d=0.872$ ) to light hydrocarbon oil ( $d=0.680-0.710$ ); yield, 80% by vol.; the initial material in a container made of quartz and by addition of the catalyst is subjected to the action of electromagnetic short waves, or ultra-short waves, obtained from 3 senders arranged symmetrically around the reaction container and contributing waves of various lengths; these senders are intermittently connected with one antenna of the two antennas with which each sender is supplied; the first antenna system gives continuous vibrations which cause ionization of the initial material, while the second causes cracking by means of intermittent vibrations.	$Al_2O_3$ .	Théophile de Borjymsky: F.P. 829,355, June 24, 1938.
Cracking process; the mineral oil, after indirect preheating through process products and direct heating in a heating coil, is evaporated, and by adding vapor is led through a cracking chamber filled with active silicates, especially Al hydroxide silicates; the cracking products are desulfurized in a second chamber at $350^\circ$ and again in a third chamber at $250^\circ$ , then refined by polymerization; the heat exchangers are inserted between chambers 1 and 2 and between chambers 2 and 3; the parts condensed by heat exchange are withdrawn before further working out of vapors.	Ni, Co, or Cu. Al hydrosilicate	Houdry Process Corporation (Pew, Jr.): U.S.P. 2,121,046, June 21, 1938.
Cracking process under increasing pressure (up to 425 kg./cc. <sup>3</sup> ). Grozny's paraffin benzine and crude oil distillate are subjected to cracking, and the influence of pressure increase upon the composition of cracking products is investigated; the increase of pressure has no essential influence upon the obtained amount of gases and benzine fractions (up to $150^\circ$ ); with increased pressure the amount of unsaturated products in the gaseous and liquid products decreases; the amount of aromatics increases considerably, and the hydrogen content in the gaseous phase decreases greatly, probably by hydrogenation reactions which are greatly accelerated by the high pressure; the possibility of a polymerization of unsaturated compounds in the liquid, as well as gaseous phase, is not excluded.		Manetkin and Gerassimow: <i>Zhur. Priklad. Khim.</i> , 11, 413-419 (1938).
Cracking of mineral oils.	To support regeneration of the catalyst the latter, consisting of aluminum silicates, is impregnated with 0.5-1% Fe, Ni, Cu, Cr, Mn and is treated before application with $H_2S$ or other volatile sulfur compounds, whereby the impregnating metals are converted into sulfides; when the catalyst becomes lame, the sulfides are converted by $H_2$ or vapor into metals or their oxides and the catalyst is regenerated by air; the oxida-	Houdry Process Corp. (Houdry): U.S.P. 2,129,693, Sept. 13, 1938.

Table 19 (Continued).

Reaction	Catalyst	Observer
	tion of the deposit on the catalyst follows then very uniformly without local superheating; when regeneration is accomplished, the oxides are again converted into sulfides and the catalyst is suitable for re-use.	
Cracking process; paraffin-containing oils for improving adhesiveness are subjected to a mild cracking under pressure above 6 atm. for 10-60 min. at 400-480° (better 440-465°) whereby the smallest amount of 180° fractions should be formed.	Brown coal, low-temperature coke, tar, or petroleum coke; blast furnace coke impregnated with sodium silicate; pumice; bauxite; (Fe-containing limonite).	Tovote: F.P. 830,194, July 22, 1938.
Cracking and reforming of hydrocarbon oils: Mid-Continent gas oil ( $d=0.8448$ , end-point about 382°) is heated, together with 316° b.p. reflux condensate from the fractionator for cracking products, in a heated spiral tube attached to a cracking chamber at 449° under 28 atm.; in another such tube a natural benzine from paraffin-base crude oil is heated with a condensate of b.p. 204-327° at 538° under 46 atm.; the products originating thereby are introduced into a coking chamber (working under 3.5 atm.) up to 40% and up to 60% in a cracking chamber; this method renders 75% benzine (Octane No. 70, end-point 204°) with respect to starting oil, and about 17 lbs. coke per barrel.		Universal Oil Products Co. (J. C. Morrell): U.S.P. 2,132,639, Oct. 11, 1938.
Cracking process (Universal Oil Products Co.) in which benzine prepared only by polymerization of the cracking gas is added to benzine directly obtained from cracking benzine, renders 85% yield of an 81-octane number benzine.	Catalyst present in two reaction chambers.	Ziegenhain: <i>Oil Gas J.</i> , <b>37</b> (No. 30), 23 (1938).
Benzine from cracking gases; T. 425-815°; pressure 14-105 atm.	A mixture of equal parts of powdered phosphate rock and fire clay (a mixture of quartz sand and water glass reduced to a paste with water and dried).	Rose, Benedum and Trees: U.S.P. 2,126,281, Aug. 9, 1938.
Benzine from cracking gases; T. 90-538°; pressure 14-84 atm.	A mixture of powdered phosphate rock and kaolin or china ton reduced to a paste, dried, pulverized, and mixed with 5-10% dried and finely divided $P_2O_5$ .	Rose, Benedum and Trees: U.S.P. 2,126,282, Aug. 9, 1938.
Cracking process; mineral oil is cracked catalytically; cracking is carried out intermittently and long enough for about 1% carbon to be precipitated on the catalyst, and then oxidized in such a manner that the temp. of the catalyst does not exceed essentially the highest cracking temp.; the method is best carried out when the catalyst is arranged around narrow tubes, cooled, or heated by corresponding agents.	Al hydrosilicates; the catalyst is self-regenerated in the reaction space.	Houdry Process Corporation (Houdry): U.S.P. 2,161,676, June 6, 1939.
Cracking of mineral oils; the mineral oil is heated in a heating spiral into which are introduced light hydrocarbons, such as heavy benzine, and gaseous hydrocarbons, such as propane and butane; after the oil has	With and without catalysts.	Texas Co. (Dearborn): U.S.P. 2,161,247, June 6, 1939.

Table 19 (Continued).

Reaction	Catalyst	Observer
reached the cracking temp. and at the end of the process it is heated in presence of suitable catalysts; the cracking products are then conducted through a cracking chamber from top to bottom, discharged and fractionated; the heavy benzine fraction thus obtained is led back into the heating spiral; furthermore, the benzinés are stabilized in a special column and thereby the hydrocarbons of the butane-propane fraction are separated from the still lower-boiling hydrocarbons and led back into the cracking zone.		
Decomposition of charcoal by water vapor (with $\text{Li}_2\text{CO}_3$ activated charcoal gives a greater degree of decomposition than if $\text{Li}_2\text{CO}_3$ activates graphite or a kind of lignite rich in volatile matter); the conversion with these catalysts is three times that of pure charcoal; the catalysts were found to influence also the velocity of establishing the water gas and the Boudouard equilibrium; the deviations of the first are caused by the thermal splitting off of $\text{H}_2$ from charcoal and by preferred primary $\text{CO}_2$ formation; in the case of Boudouard's equilibrium, pure charcoal gives the best results.	$\text{Li}_2\text{CO}_3$ ; reverse is the action of additions such as $\text{K}_2\text{CO}_3 + \text{CuO}$ or $\text{K}_2\text{CO}_3 + \text{Co}_3\text{O}_4$ because of the difference in the procedure of the catalytic partial reactions in the case of single carbon materials; $\text{Ni}_2\text{O}_3$ , $\text{ThO}_2$ , $\text{CaO}$ , $\text{ZnO}$ and $\text{NaVO}_3$ used in various combinations; the catalysts act only at low temperatures; they hinder further the decrease in the amounts of gas produced (at constant temp. with time).	Kröger and Willenberg: <i>Z. Elektroch.</i> , <b>44</b> , 524-536 (1938).
Cracking of hydrocarbon oils.	Coking products of brown coal, also of optional mineral coal of especial piece solidity; the ash is removed after activation with water vapor, extraction with water, treatment with dilute acid ( $\text{H}_2\text{SO}_4$ ), and re-extraction with water vapor or water gas or both, reduced and finally washed with water.	Deutsche Erdöl A.-G. (Schick and Emilius): G.P. 677,188, Kl 12i, June 21, 1939; refer also to G.P. 645,222 (1934) F.P. 756,922 (1934).
Cracking of slate and brown coal tar at ordinary pressure in the presence of $\text{H}_2$ (with increase in the yield the cracking oils show lower boiling point and smaller content of phenol than when cracking takes place without lime and $\text{H}_2$ ).	Lime.	Barlot: <i>Mat. grasses</i> , <b>31</b> , 14-15 (1939).
Cracking of Rumanian wax (ozocerite) at ordinary pressure; the yield of liquid crude products decreases with an increase in $\text{AlCl}_3$ ; the same is true for the yield of crude benzine and kerosene; the highest yield is obtained with 2% $\text{AlCl}_3$ at 150-270°.	$\text{AlCl}_3$ (2-25%).	Otin and Catrutz: <i>Petroleum</i> , <b>35</b> , 561-67 (1939).
Cracking process; hydrocarbon vapors are led through the catalyst at 410-480°; special heating arrangements permit regulating the reaction temp.; to assure best yields of benzinés, the cracking must be discontinued when 15 g. coke are deposited on one liter of catalyst; thus, in less than 20 min. a considerable amount of oil vapors (calculated as liquid oil) is led over the catalyst corresponding to half the volume of the catalyst, after which the catalyst is regenerated by care-	Highly active Al silicate (each particle of the catalyst should be not more than one inch from the medium, which regulates the reaction temp.; therefore the contact masses are arranged in many thin layers one on top of another).	Houdry Process Corp. (Houdry): U.S.P. 2,161,677, June 6, 1939; Belg. P. 429,543, March 22, 1939.

Table 19 (Continued).

Reaction	Catalyst	Observer
<p>ful oxidation at a temp. not higher than 595°; the streaming velocity of oil vapors over the catalyst must be regulated with accuracy, for this serves a special formula.</p>		
PART VI		
Catalytic Hydration in Organic Chemistry		
Table 1. Catalytic Hydration of Ethylene.		
Reaction	Catalyst	Observer
Hydration of ethylene to form ethyl alcohol	Non-catalytic.	(Discovered by Hennem, a co-worker of Faraday).
(1) $C_2H_4 + HOSO_2H = C_2H_5 \cdot OSO_2H$	Mo, W, V and U acids in the presence of Hg catalyst.	Berthelot: <i>Compt. rend.</i> , <b>40</b> , 102 (1855).
(2) $C_2H_4OSO_2H + H_2O = C_2H_5OH + H_2SO_4$		Fritzsche: <i>J. Soc. Chem. Ind.</i> , <b>40</b> , T86 (1921).
		Lebeau and Damiens: <i>Compt. rend.</i> , <b>156</b> , 557 (1913).
		deLoisy: <i>Compt. rend.</i> , <b>170</b> , 50 (1920).
Hydration of ethylene to ethyl alcohol.	Fe, Cu, Co, Ni, Ce, Mn, Cr, Sn, Au.	G.P. 414,913 (1925). U.S.P. 1,574,796 (1926). F.P. 519,568 (1921).
Hydration of ethylene, using $H_2SO_4$ to which are added foam promoting agents, such as olive oil, tetrahydronaphthalene, etc.; in the conversion of ethylene to ethyl alcohol a stronger $H_2SO_4$ is used for adsorption of ethylene than for other olefins; to facilitate adsorption of gases 0.1% of olive oil or tetrahydronaphthalene is added so that a foam is produced.	$AgSO_4$ .  1% $AgS$ .  Salts of Fe, Co, Ce, Mn, Cr, Bi, Sn, Au; complex salts of the type of ferric cyanides are used as catalysts for the adsorption of $C_2H_4$ .	I. G. Farbenindustrie A.-G. (Werk Leverkusen): <i>Ber. Ges. Kohlentech.</i> II, 5 (1926).  <i>Ber. Ges. Kohlentech.</i> I, 210, 224 ( ). G.W.F., <b>70</b> , 97 (1927).  G.P. 414,913 (1920). E.P. 152,494 (1920). E.P. 152,495 (1920). E.P. 324,897 (1930). E.P. 323,748 (1930).
Conversion of ethylene to ethyl alcohol; instead of diluting the ethyl sulfuric acid obtained with water and subjecting to distillation, ethylene is adsorbed by $H_2SO_4$ diluted with a solution of ammonium sulfide over the catalyst, treated with ammonium hydroxide and then the alcohol formed distilled off; $(NH_4)_2SO_4$ is crystallized out and the mother liquor is used again for dilution of $H_2SO_4$ .	$K_2FeCN_6$ .	N. V. Bataafsche Petroleum Maatschappij: E.P. 341,167 (1930).
A direct hydration of ethylene hydrocarbons; ethylene together with water vapor is passed at 150° through a tube containing catalysts; 15-20% alcohol is obtained.	Pt, Au, Ag, Cu, Fe, Ni, Co, Cr, Ta, V, W, Mo and Mn and their respective oxides; $WO_3$ on active charcoal.	Sherlock and Swann: <i>Ind. Eng. Chem.</i> , <b>22</b> , 1048 (1930). N. V. Bataafsche Petroleum Maatschappij: Brit. P. 335,551 (1930).
Conversion of homologs of ethylene into their corresponding alcohols occurs more readily because they are adsorbed more easily and require a weaker $H_2SO_4$ for adsorption.		Markowitch and Moor: <i>Neft-yanoé Khos.</i> , <b>19</b> , 604 (1930).
Condensation of 1 vol. ethylene and 1 vol. water vapor to ethyl alcohol.	Silica gel, clay, $Al_2O_3$ (greatest effect) ammonia alum when calcined gives a residue of alumina.	Wakscheidt and Koganowa: <i>Trudy Vsesoyuz. Mendeleev. S'ezda</i> II, 1, 738 ( ).
Condensation of ethylene with water to ether; T., 250-360°; pressure, 10-60 atms.	$Al_2O_3$ .	Brown and Odell: U.S.P. 1,873,536 (1932).

Table 1 (Continued).

Reaction	Catalyst	Observer
Condensation of olefins with water. (1) $2C_2H_4 + H_2O = (C_2H_5)_2O$ —ether (1) (2) $C_2H_4 + H_2O = C_2H_5OH$ —alcohol (2) (1) T. 150–350°, 25 atm. (1) 3 vol. $C_2H_4$ and 1 vol. $H_2O$ vapor heated to 200°.	(1) Bisulfates, chlorides of Ca, Zn, Mn (hygroscopic salts) precipitated on silica gel. (2) Metaphosphates of alkalis or alkaline earths on silica gel.	(1) Dreyfus: F.P. 745,084 (1933) (2) Dreyfus: E.P. 407,722 (1933).
Hydration of ethylene in the preparation of ethyl alcohol at 150°; ethyl alcohol formed with a yield of 2% without marked side reactions in one operation.	Active charcoal impregnated with 70% $H_2SO_4$ with the addition of $Ag_2SO_4$ ; fatigue of the catalyst a disadvantage.	Balandin and Neswichsky: <i>Uchenye Trudy Moskov. Univ.</i> , 2, 233–235 (1934).
Hydration of ethylene in vapor phase; temp., 320°, 350°, 378°.	$Al_2O_3$ contacts (treatment with air at about 500° increases the stability of activity); $WO_3$ , $H_3PO_4$ or $H_3BO_3$ may be added.	Bliss and Dodge: <i>Ind. Eng. Chem.</i> , 29, 19–25 (1937).
Hydration of aliphatic hydrocarbons, e.g., $C_2H_4$ to alcohol and ether.	Alkali oxides, alkaline-earth oxides, $ThO_2$ , $Al_2O_3$ , $WO_3$ , $SiO_2$ , $TiO_2$ , $ZrO_2$ and $Cr_2O_3$ .	
Hydration of ethylene to alcohol.	Natural malachite or basic $CuCO_3$ treated with so much $H_3PO_4$ that $CuHPO_4$ is formed (the paste obtained may be mixed with carbohydrates and placed on a carrier and dried).	Wanscheidt and Kaganowa: Russ. P. 50,469, Feb. 28, 1937.

Table 2. Catalytic Hydration of Propylene and Amylene.

Reaction	Catalyst	Observer
Hydration of amylene for preparing dimethylethyl carbinol (yield, 90%).	$H_2SO_4$ .	Adams, Kamm and Marval: <i>J. Am. Chem. Soc.</i> , 40, 1950 (1918).
Hydration of higher olefin hydrocarbons: propylene, butylene and amylene obtained by cracking of petroleum hydrocarbons under diminished pressure at 500–600°; then the gas with olefin content of about 8–10% is treated at atmospheric or slightly elevated pressure with 86–93% $H_2SO_4$ ; (d. 1.80–1.82) at 30°, then it is split similar to ethyl sulfuric acid into propyl, isobutyl and amyl alcohol.	Ni.	Standard Oil Co.: U.S.P. 1,594,823 (1926).
Hydration of propylene and butylene to corresponding alcohols, temp. 170–250° and 20–40 atms.	Bi salts or salts of heavy metals of the first group.	I. G. Farbenindustrie A.-G.: E.P. 324,897 (1930); refer also to: E. P. 249,834 (1926), and F.P. 612,329 (1926).
Hydration of propylene to isopropyl alcohol at 110° has maximum conversion; addition of water vapor does not improve the yield of alcohol, but assures a continuous process.	Ag has no catalytic effect; 64% $H_2SO_4$ has greatest effect.	Gutyrga and Buinitzkaja: <i>Zhur. Priklad. Khim.</i> , 10, 882–887 (1937); <i>Azerbaidzshanskoe Neftyanoe Khos.</i> , 17, No. 1, 50–58 (1937); (Refer to C. 1937 II, 2292).
Hydration of olefins; temp. and pressure chosen so that the olefin is held in a liquid phase; $C_3H_6$ at 80° and 40 atm. with 30–40% acid to isopropyl alcohol; $C_4H_8$ at 100°, 15–20 atm. with 20–40% $H_2SO_4$ to isobutyl alcohol; trimethylethylene at 120°, 10–15 atm. with 15% $H_2SO_4$ to tertiary amyl alcohol.	Diluted polybasic mineral acids.	Distillers Co., Ltd.: (Stanley and Jonell): E.P. 466,439, June 24, 1937.



Table 3. Catalytic Hydration of Unsaturated Hydrocarbons (Olefins).

Reaction	Catalyst	Observer
Hydration of olefins.	Au, Ag, Cu, Fe, Ni, Co, Cr oxalates; V, W, Mo carbonyls or metal salts with weak inorganic acids.	N. V. Bataafsche Petroleum Maatschappij; E.P. 335,551 (1930).
Hydration of unsaturated hydrocarbons, such as olefins or aliphatic hydrocarbons brought into reaction with water vapor at temperatures over 100° and increased pressure of 10 atm.; depending upon the amount and the relationship between the hydrocarbons and water, ether or alcohols are chiefly obtained; from ethylene, alcohols and ether; from styrol, methylphenyl carbinol and phenylethyl alcohol are produced.	Metallic oxides, such as Al, Th, Ti, W, Cr oxide.	Brown and Odell; U.S.P. 1,907,317, May 2, 1933.
Hydration of olefins with water to form alcohols; T. 150-300°; 20-50 atm.	(1) Alkali or alkaline earth metaphosphates precipitated on kieselguhr; di- and poly-metaphosphates may be used. (2) Bisulfates, pyrosulfates or chlorides of Ca, Zn, Mg as melts or aqueous solutions precipitated on silica gel.	Dreyfus; (1) E.P. 407,722 (1933); (2) F.P. 745,084 (1933); E.P. 389,136 (1932).
T. 150-350°; elevated pressure.		
Condensation or hydration of olefins; T. 150-500° at ordinary and elevated pressure.	ZnO, CdO containing Al <sub>2</sub> O <sub>3</sub> .	Chaffette; F.P. 750,053 (1933).
Hydration of olefins to alcohols; T. 125-130°, 25-900 atm.	Volatile halide compounds (hydrogen halide acids) and active substances, such as coke, silica gel.	Dupont (Larson); U.S.P. 2,014,740 (1935).
Hydration of olefins to prepare alcohols and esters.	Hydration catalysts: H <sub>2</sub> SO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub> ; halides of Al, Cd, Zn; acetic or oxalic acid.	Standard Oil Development Co.; F.P. 786,081, Aug. 26, 1935.
Hydration of olefins with sulfuric acid (water content measured so that alkyl sulfuric acid is formed).	Oxides of Cu, Ag, Pb Bi, Au.	Usine de Mell Société Anonyme; F.P. 799,704, Aug. 18, 1936.
Hydration of olefins to form alcohols with H <sub>2</sub> SO <sub>4</sub> or H <sub>3</sub> PO <sub>4</sub> (50%); high pressures and temperatures; above the c.p. of the acid solution and above the c.p. at which corrosion of the lead coating takes place.	Lead coating on the inner walls of the closed vessel.	Air Reduction Co., Inc. (Metzger); U.S.P. 2,087,290, July 20, 1937.
Hydration of olefins to prepare alcohols; T. 175-375°; high pressure, 35-210 atm. with a far-reaching utilization of heat used for the reaction in the circle; the alcohol formed is washed out from the reaction mixture containing by-products (ether) through hot water preheated to the reaction temp. and under the same pressure as that of reaction gases.	Catalysts.	Carbide and Carbon Chemicals Corp.; F.P. 828,684, May 25, 1938.
Hydration of olefins to prepare aliphatic alcohols and ether (C <sub>2</sub> H <sub>5</sub> OH and (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O) using water or water vapor; high temp. and pressures.	Catalysts containing boron and halogen; likewise may be used adsorbing acting substances such as pumice, silica gel, coke, which may be also activated; especially suitable are fluorine compounds of B, such as BF <sub>3</sub> , BF <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> .	Dupont; E.P. 486,783, July 7, 1938.
Hydration of olefins to alcohols (in gaseous or liquid phase); in gaseous phase the initial material is led with advantage over adsorbing acting substances such as pumice, silica gel, active carbon, which may be impregnated also with activating substances; preparation of ethyl and propyl alcohol.	Water-containing boron halide alone or activated by other substances, such as Ni, NiO, HgO.	E. I. du Pont de Nemours & Co. (Loder); U.S.P. 2,135,455, Nov. 1, 1938.

Table 4. Catalytic Hydration of Acetylene.

Reaction	Catalyst	Observer
Hydration of acetylene to acetaldehyde; yield of acetaldehyde 4-5% of the theoretical value.	Hg salt solution in the presence of an acid; hot HgO containing 45% H <sub>2</sub> SO <sub>4</sub> .	Kutscheroﬀ: <i>Ber.</i> , <b>14</b> , 1540 (1881). Erdmann and Köthner: <i>Z. anorg. Chem.</i> , <b>18</b> , 48 (1898). Hofmann: <i>Ber.</i> , <b>32</b> , 874 (1899). Farbwerken vorm. Meister Lucius and Brünig: G.P. 286,400 (1915). G.P. 292,818 (1916). G.P. 293,070 (1917). G.P. 299,466 (1917). G.P. 299,467 (1917).
Hydration of acetylene to acetaldehyde (C <sub>2</sub> H <sub>2</sub> obtained from CaC <sub>2</sub> is freed completely from H <sub>2</sub> SO <sub>4</sub> and H <sub>2</sub> PO <sub>4</sub> ); a large excess of C <sub>2</sub> H <sub>2</sub> must be taken and sufficiently high temp. of H <sub>2</sub> SO <sub>4</sub> ; to avoid polymerization of the acetaldehyde formed it should be removed at once from the sphere of action of H <sub>2</sub> SO <sub>4</sub> ; the hydration of C <sub>2</sub> H <sub>2</sub> in the gaseous phase by water vapor at high temp. has not yet found broad application.	Salts of Hg in dilute (15-25%) H <sub>2</sub> SO <sub>4</sub> (partial reduction of Hg salts to metal because of side reactions necessitates the use of a counteracting agent such as salts of Fe oxide, re-oxidizing the suboxide of Hg to oxide; the Fe suboxide is oxidized in its turn by HNO <sub>3</sub> ).	Société Chimie des Usines du Rhône: G.P. 322,746 (1920). G.P. 309,103 (1920). G.P. 309,104 (1920). Chemische Fabrik Rhenania: G.P. 365,285 (1922). G.P. 369,515 (1923). F.P. 524,958 (1921). Plauson: G.P. 350,493 (1922). Swiss P. 97,057 (1922). Swiss P. 98,557 (1922). U.S.P. 1,471,058 (1923).
Hydration of acetylene in a gaseous phase, e.g., by the action of water vapor at high temp.	Hg salt + Fe <sub>2</sub> O <sub>3</sub> which oxidizes the suboxide of Hg into the oxide by reducing the Fe <sub>2</sub> O <sub>3</sub> into the suboxide of Fe.	Union Carbide Co.: U.S.P. 1,247,270 (1918). G.P. 309,103 (1919). G.P. 309,104 (1919).
Hydration of acetylene with water vapor to acetic acid; T. 250-300°; with the gases is admixed air or oxygen for oxidation of acetaldehyde.	Small amount of acetic, sulfuric, phosphoric, nitric acid or organic sulfo acid (acid-proof steel used as container).	F.P. 479,656 (1919). E.P. 156,152 (1920).
Hydration of acetylene to acetic acid; T. 300-400°; in mixture oxidized with air.	Salts of Mo, W and Cr oxide.	Wohl: E.P. 154,579 (1920).
Hydration of acetylene to acetaldehyde.	Active charcoal (from nut shells) impregnated with maximum 1% HgO or other Hg cpds. or salts or oxides of Zn, Cu, Mo, Fe, Ni, Sn, Al, or Pb.	Bender: U.S.P. 1,355,299 (1920).
Hydration of acetylene to acetaldehyde; T. 400-420°.	Hydrated Fe oxide, Al, Hg, or Si hydrates (a complete dehydration should be avoided).	Deutsche Gold- und Silberscheideanstalt: G.P. 334,357 (1920). F.P. 518,086 (1920). Swiss P. 92,114 (1922). Swiss P. 92,887 (1922). Scheller: U.S.P. 1,244,901, Oct. 30, 1917. U.S.P. 1,244,902.
Hydration of acetylene to acetone; 1 vol. C <sub>2</sub> H <sub>2</sub> and 40 vol. water vapor; T. 450°; yield 40% of used acetylene converted into acetone and 5-10% other ketones and aldehydes.	Fe oxide.	Deutsche Gold- und Silberscheideanstalt: Swiss P. 94,225 (1923). Aust. P. 88,631 (1922). Aust. P. 88,632 (1922).
Hydration of acetylene to acetaldehyde; T. 400-420°.	Fe ore and Zn vanadate.	Wohl: <i>Chem. Ztg.</i> , <b>46</b> , 863 (1922).
Hydration of acetylene to acetone.	ThO <sub>2</sub> and double salts of Th and alkali or alkaline earths.	E.P. 192,392 (1922). F.P. 561,377 (1923).
Hydration of acetylene to acetone; 1 p. C <sub>2</sub> H <sub>2</sub> and 2-5 p. H <sub>2</sub> O vapor; T. 350-450°.	K <sub>2</sub> Th(CO <sub>3</sub> ) <sub>2</sub> (double salt or simple Th oxide).	Elektrizitätswerke Lanza: E.P. 192,392 (1922). F.P. 561,377 (1923). Swiss P. 102,276 (1924).
Hydration of acetylene to acetic acid; 130 p. C <sub>2</sub> H <sub>2</sub> and 80-100 p. O <sub>2</sub> ; T. 50-100°; yield claimed to be quantitative (a mixture of 400 p. acetic acid and 100 p. H <sub>2</sub> O).	50 p. HgNO <sub>3</sub> +10 p. CeO <sub>2</sub> ; the Hg salt is the hydration catalyst; CeO <sub>2</sub> accelerates oxidation of acetaldehyde by O <sub>2</sub> .	Dreyfus: G.P. 409,947 (1925). U.S.P. 1,361,974 (1920). F.P. 497,656 (1919). F.P. 489,688 (1920). F.P. 20,217 (1919). F.P. 20,818 (1919). F.P. 22,282 (1920).

Table 4 (Continued).

Reaction	Catalyst	Observer
Hydration of acetylene with water vapor; T. about 400°; 4-15 space p. H <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> .	Holzverkohlung A.-G.: F.P. 642,111 (1929).
Hydration of acetylene with water vapor, and hydrogenation to ethyl alcohol.	(1) ZnO on silica gel; T. 380°; H <sub>2</sub> added; (2) Ni contact; T. 200°.	I. G. Farbenindustrie A.-G.: F.P. 681,839 (1930).
Hydration of acetylene to acetone; C <sub>2</sub> H <sub>2</sub> : H <sub>2</sub> O vapor, 1 : 10; T. 400°; good yield of acetone.	ZnO.	I. G. Farbenindustrie A.-G.: E.P. 330,350 (1930).
Hydration of acetylene yields are smaller than those reached in the liquid phase where almost 100% with respect to C <sub>2</sub> H <sub>2</sub> is obtained.	Fe salts with Cr acids or W or Si acids.	I. G. Farbenindustrie A.-G.: G.P. 504,862 (1930); refer also to U.S.P. 1,355,299 (1921).
Hydration of acetylene with water vapor to acetone; average yield 90%; T. 400-410°.	Porous charcoal, e.g., coke, charcoal, active charcoal, charged with Zn, Cd, Cr (Fe free), molybdic acid, tungstic acid, vanadic acid, etc.; these contacts are not sensitive to poisons present in crude acetylene; e.g., 200 g. highly active charcoal in grains impregnated with an aqueous solution of 35 g. Zn. acetate and 10 g. Mn acetate.	Deutsche Gold- und Silberscheideanstalt (Walter and Schulz): G.P. 577,705 (1933). G.P. 584,517 (1933). U.S.P. 1,892,742 (1932).
Hydration of acetylene 2-pentene is accompanied by polymerization (to a certain extent); the ketone mixture obtained consists of 52% diethyl ketone; by hydration of acetylenes of the formula: CH <sub>3</sub> C : C · R the reaction ability of C atom bound to R increases with the length of the alkyl chain.	80% H <sub>2</sub> SO <sub>4</sub> .	Mowat and Smith: <i>J. Chem. Soc.</i> , 1938, 19-22.
Hydration of acetylene.	Hg salt + Fe <sub>2</sub> O <sub>3</sub> .	
Hydration of acetylene.	Pt, Au, Ag, Cu, Fe, Ni, Co, Cr, Ta, V, W, Mo and Mn, or their oxides + WO <sub>3</sub> .	
Hydration of alkyl acetylene to ketones, such as 2-hexanone obtained from hexene, 2-heptanone from 1-heptene and 2-octanone from 1-octene; T. 60°; time, 1 hr.; after adding 41 g. hexene the temp. was maintained for 3 hrs.; for heptene, T. 80°.	Small amount of HgSO <sub>4</sub> and H <sub>2</sub> SO <sub>4</sub> in dilute methanol, acetic acid or acetone; 1 g. HgSO <sub>4</sub> + 1 g. H <sub>2</sub> SO <sub>4</sub> in 150 g. 70% methanol or 70% acetone as well as 50 g. 60% acetic acid.	Thomas, Campbell and Hennion: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 718-720 (1938).

Table 5. Catalytic Hydration of Various Organic Compounds.

Reaction	Catalyst	Observer
Hydration of phthalic acid anhydride (crude product of catalytic oxidation of naphthalene); T. 300-450° to form benzoic acid.	Activated Fe oxide, Zn oxide, CaCO <sub>3</sub> .	I. G. Farbenindustrie A.-G.: G.P. 445,565 (1927).
Hydration of phthalic acid anhydride; T. 400°. T. 390-400°. T. 330-360°.	CaCO <sub>3</sub> . Al <sub>2</sub> O <sub>3</sub> . Fe <sub>2</sub> O <sub>3</sub> activated by NiO or CuO.	
Hydration of turpentine oil to terpine hydrate.	Dilute HCl in presence of kieselguhr or silicic acid.	Kaminski: Russ. P. 15,285 Kaminski and Levy: Russ. P. 15,291.
Hydration of acetaldehyde to acetone; T. 350-500°.	Zn or Zn compounds containing Al <sub>2</sub> O <sub>3</sub> or bauxite (high streaming velocity to prevent decomposition).	I. G. Farbenindustrie A.-G.: E.P. 313,897 (1929).
Hydration of dimethyl ether and water; T. below 400°.	Al <sub>2</sub> O <sub>3</sub> (hydrating catalyst) or silica gel.	Arnold and Lazier: Can. P. 315,875 (1931).

Table 5 (Continued).

Reaction	Catalyst	Observer
Hydration of ethyl ether; 40% of ether converted into acetone, 10% into ethyl alcohol and 18% into ethylene.	To the hydroxide prepared from 100 g. of Al was added 100 g. of finely dispersed Fe oxide and 12 g. Mg. oxide, filtered and dried at 120–130°.	Kagan, Kossinskaja and Tschernizow: <i>Zhur. Obshchei Khim.</i> , <b>3</b> , 65, 337–344 (1933).
Hydration of ether vapors with water vapor to acetone; T. 400–500°.	Al(OH) <sub>3</sub> containing Fe, Mg or Ca oxides.	Kagan: Russ. P. 39,785.
Hydration of mesityl oxide and simultaneous splitting into acetone; T. 200–300°; 19–32% of mesityl oxide hydrolyzed.	Al <sub>2</sub> O <sub>3</sub> or silicic acid gel (high hydrolyzing ability).	Zangirolami: <i>Ann. chim. applicata</i> , <b>24</b> , 347 (1934).
Hydration of ethyl alcohol or acetaldehyde to acetone; T. 420°; 90 p. H <sub>2</sub> O and 10 p. ethyl alcohol or acetaldehyde; 90% theoretical yield.	200 g. active coal impregnated with 50 g. ZnO in dilute acetic acid.	Deutsche Gold- und Silberscheideanstalt (Walter): G. P. 622,493 (1936).
Hydration of $\alpha$ -pinene by acetic acid to bornyl acetate + 25% isobornyl acetate.	Japanese acid ton (the dehydrated ton adsorbing acetic acid would lead to the formation of acetyl-silicic acid; an analogy is drawn between the activation of acetic acid through the ton and its activation by H <sub>2</sub> SO <sub>4</sub> ).	Kuwata: <i>J. Soc. Chem. Ind. Japan</i> , <b>39</b> , 392B–394B (1936).
Hydration of hydrocarbons.	CuO + WO <sub>3</sub> on active charcoal.	
Hydration or dehydration.	Hydrogen ions of acids and their aqueous and alcoholic solutions.	
Hydration of unsaturated compounds, e.g., reversible hydration of crotonic acid to $\beta$ -oxybutyric acid in 1.06–2.06N HClO <sub>4</sub> solution (ion strength 2.06 at 90.03° and 111.31 $\pm$ 0.05°); the reaction is of the first order; the equilibrium constant is 5.0 at 90° and 3.4 at 111°; activation energy for hydration is 38.0 kcal.; for dehydration, 48.1 kcal.; the reaction heat is 10.1 k. cal.		Pressman and Lucas: <i>J. Am. Chem. Soc.</i> , <b>61</b> , 2271–77 (1939).

## PART VII

## Catalytic Dehydration in Organic Chemistry

Table 1. Catalytic Dehydration of Methyl Alcohol (Industrial Process).

Reaction	Catalyst	Observer
Dehydration of CH <sub>3</sub> OH; T. 750–800°.	Glowed kaolin.	Deyman (1795); refer also to <i>Bull. soc. chim.</i> , <b>2</b> , 1000 (1935).
Dehydration of methyl, ethyl, propyl and butyl alcohols with NH <sub>3</sub> .	W <sub>2</sub> O <sub>5</sub> , WO <sub>3</sub> , silica gel prepared at 465°; Al <sub>2</sub> O <sub>3</sub> on pumice; a mixture of silica gel and NiO; a mixture of silica gel and ThO <sub>2</sub> ; CeO on pumice.	Brown and Reid: <i>J. Phys. Chem.</i> , <b>28</b> , 1067 (1924).
Dehydration of methyl alcohol.	Cu.	Ghosh and Chakravarty: <i>Quart. J. Indian Chem. Soc.</i> , <b>2</b> , 142–149 (1925).
Dehydration of two different alcohols; 25 g. $\beta$ -naphthol + 10 cc. methyl alcohol; ether yield, 50%.	3 g. Silicic acid gel (a silica gel precipitated with HCl or ammonium nitrate especially active).	Korolew: <i>Zhur. Khim. Prom.</i> , <b>4</b> , 547 (1927).
Dehydration of non-aqueous methyl alcohol to methyl ether in a quantitative yield; T. 320–360°.	Al <sub>2</sub> O <sub>3</sub> .	Adkins and Perkins: <i>J. Phys. Chem.</i> , <b>32</b> , 221 (1929).
Dehydration of methyl alcohol to dimethyl ether; T. 250–370°.	Al <sub>2</sub> O <sub>3</sub> ; glassy Al <sub>2</sub> O <sub>3</sub> activated with small amounts of oxides from groups 1, 6, 7 and 8.	Ipatieff: "Aluminum as a Catalyst in Organic Chemistry," p. 25, Leipzig, 1929. I. G. Farbenindustrie A.-G.: E.P. 313,426 (1929).

Table 1 (Continued).

Reaction	Catalyst	Observer
Dehydration of methyl alcohol and phenol to anisol.	Active bleaching earth.	RheinischeKampfer Fabrik (Schöllkopf): F.P. 681,049 (1930). E.P. 319,205 (1929).
Dehydration of methanol and ethanol to methyl ethyl ether and its rearrangement giving normal propanol: $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH} \rightarrow$ $\begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{C}_2\text{H}_5 \end{array} \text{O} \rightarrow \text{C}_2\text{H}_5\text{CH}_2\text{OH}$ similarly, $\text{CH}_3\text{OH} + \text{CH}_3\text{OH} \rightarrow$ $\begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CH}_3 \end{array} \text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH}$ production of ethanol through dimethyl ether as intermediate compound.		Frolich: <i>Ind. Eng. Chem.</i> , <b>23</b> , 111 (1931).
Dehydration of methyl alcohol to dimethyl ether; T. 175-500°; atmospheric pressure or 200 atm.	$\text{Al}_2\text{O}_3$ or silicic acid gel.	Dupont (Woodhouse): E.P. 403,402 (1933). U.S.P. 2,014,408 (1935).
Dehydration of methanol.	Glowed kaolin; $\text{H}_2\text{O}$ content, 1 %.	Larin and Tscherepnjew: Russ. P. 41,504, Feb. 28, 1935.

Table 2. Catalytic Dehydration of Ethyl Alcohol.

Reaction	Catalyst	Observer
Dehydration of ethyl alcohol to ethylene; T. 380-400°; yield of ethylene, 90%.	$\text{Al}_2\text{O}_3$ (obtained by precipitating $\text{Al}(\text{OH})_3$ from Al salt solutions with alkali, washing the hydroxide and drying at 300°, removing by washing the adsorbed alkali and drying again).	Gregoriev: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>33</b> , 173 (1901). Ipatieff: <i>J. prakt. Chem.</i> , <b>67</b> , 421 (1903). Walter: G.P. 168,291 (1907). F.P. 360,785 (1907).
Dehydration of ethyl alcohol to olefins to ethylene; T. 280°.	$\text{Al}_2\text{O}_3$ .	Badische Anilin- und Soda Fabrik: (used the method on a large scale). Sabatier and Maible: <i>Compt. rend.</i> , <b>147</b> , 106 (1908). Senderens: <i>Compt. rend.</i> , <b>148</b> , 227 (1909).
Dehydration of ethyl alcohol; T. 240-260°; yield of ether, 83.5%.	Precipitated alumina heated below red glow.	Senderens: <i>Compt. rend.</i> , <b>148</b> , 288 (1909); <i>Bull. soc. chim.</i> (4), <b>5</b> , 480 (1909).
Dehydration of ethyl alcohol to ethylene.	$\text{Al}_2\text{O}_3$ or coke impregnated with $\text{H}_3\text{PO}_4$ .	U.S. Industrial Alcohol Co. (Backhaus): U.S.P. 1,402,336 (1921).
Dehydration of ethyl alcohol.	$\text{ThO}_2$ and $\text{WO}_3$ .	U.S. Industrial Alcohol Co. (Backhaus): U.S.P. 1,402,336 (1921). U.S.P. 1,421,640 (1922).
Dehydration of ethyl alcohol and ammonia; T. 300-350° C; yield 53% by-product ethyl ether and ethylene; $\text{NH}_3$ : $\text{C}_2\text{H}_5\text{OH}$ = 1 : 2.	Alumina.	Smolmsky: <i>Roczniki Chem.</i> , <b>1</b> , 232 (1923).
Dehydration of ethyl alcohol.	$\text{ZnO}$ .	Lazier and Adkins: <i>J. Am. Chem. Soc.</i> , <b>47</b> , 1718-1722 (1925).
Dehydration of ethyl alcohol.	$\text{ThO}_2$ .	Tweedy: <i>Chimie &amp; industrie</i> , <b>45</b> 77-80, 157-159 (1925).
Dehydration of ethyl alcohol to ethylene.	Glassy alumina.	I. G. Farbenindustrie A.-G.: (Mittasch and Michael): G.P. 454,353 (1928).
Dehydration of ethyl alcohol.	Glassy clay with activators: Ni, Cu, Ag, $\text{CuO}$ , $\text{CuO} + \text{Ag}_2\text{O}$ , $\text{Cr}_2\text{O}_3$ , $\text{MnO}$ , $\text{ZnS}$ , $\text{CoS}$ , also selenides and phosphides.	I. G. Farbenindustrie A.-G.: E.P. 313,426, July 11, 1929.
Dehydration of ethyl alcohol.	$\text{Al}_2\text{O}_3 + \text{CuO}$ . $\text{CuO} + \text{Ag}_2\text{O}$ . $\text{Al}_2\text{O}_3 + \text{NiO}$ .	I. G. Farbenindustrie A.-G.: E.P. 313,426, July 11, 1929. E.P. 326,185, Feb. 27, 1930.
Dehydration of ethyl alcohol.	$\text{Al}_2\text{O}_3 + \text{CuSO}_4$ . $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ .	I. G. Farbenindustrie A.-G.: F.P. 679,998, 1930.

Table 2 (Continued).

Reaction	Catalyst	Observer
Dehydration of non-aqueous ethyl alcohol; in non-catalytic processes alcohol is lost and sulfuric acid wasted (industrial process).	$\text{Al}_2\text{O}_3$ impregnated with a solution of $\text{CuSO}_4$ and adding dropwise a solution of $\text{Na}_2\text{CO}_3$ until the whole Cu is converted into $\text{CuCO}_3$ , washed and dried; $\text{Al}_2\text{O}_3$ and Cr anhydride.	Yatkar and Watson: <i>Ind. Eng. Chem.</i> , <b>45T</b> , 168 (1928). P.P. 679,998 (1930).
Dehydration of ethyl alcohol to ethylene; T. up to $400^\circ$ .	Magnesium phosphate dispersed on fine-grained coke (100 p. Mg salt, 1 p. $\text{H}_3\text{PO}_4$ in 100 p. $\text{H}_2\text{O}$ heated to $60^\circ$ by an air stream, dispersed on 100 p. coke).	I. G. Farbenindustrie A.-G.: E.P. 326,185 (1930).
Dehydration of ethyl alcohol.	Anhydrous $\text{K}_2\text{CO}_3$ .	Pester, Abbata and Maroso: <i>Rev. faculad quim. ind. agr. (Univ. nac. litoral, Santa Fe, Argentina)</i> , <b>2</b> , 141-148 (1932).
Dehydration of ethyl alcohol to ethylene.	Birch wood + $\text{Al}_2\text{O}_3$ .	Adadurov and Kraini: <i>Zhur. Fiz. Khim.</i> , <b>5</b> , 136-44 (1934).
Dehydration of ethyl alcohol. (1) $\text{C}_2\text{H}_5\text{OH} + 2\text{H}_2\text{O}$ (under 0.5%) + Ca $\rightarrow$ $\text{Ca}(\text{OH})_2 + \text{H}_2$ (2) $2\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ (under 0.2%) + Ca $\rightarrow$ $\text{Ca}(\text{C}_2\text{H}_5\text{O}_2) + \text{H}_2$ (3) $\text{Ca}(\text{C}_2\text{H}_5\text{O})_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + 2\text{C}_2\text{H}_5\text{OH}$	Metallic Ca.	Smith and Getz: <i>Ind. Eng. Chem., Anal. Ed.</i> , <b>9</b> , 100-102, (1937).
Dehydration of ethyl alcohol to ethylene.	$\text{Al}_2\text{O}_3$ contact (with decreasing water content the amount of ethylene formed increases).	Spinoglio: <i>Atti mem. accad. sci. Padova</i> , <b>51</b> , 25 (1934-35).
Dehydration of ethyl alcohol.	Alumina with 5.5% by weight of $\text{H}_2\text{O}$ .	Munro and Horn: <i>Can. J. Res.</i> , <b>12</b> , 707-710 (1935).
Dehydration of ethyl alcohol; T. $318^\circ$ and $450^\circ$ ; the ratio of $\text{C}_2\text{H}_4$ : $\text{C}_2\text{H}_5\text{OH}$ depends on the water content of the catalyst; previous experiments at $250^\circ$ showed no influence of water content in the catalyst.	Alumina; with catalysts of high initial $\text{H}_2\text{O}$ content the reaction course changes during use; catalysts freed from water by glowing are not inactive but as a result of decreased activity favor the formation of ethyl ether.	Alexander, Horn and Munro: <i>Can. J. Res.</i> , <b>15</b> , (B), 438 (1937).
Dehydration of alcohol to olefin; amyl alcohol is dehydrated 3.5 times more easily than ethyl alcohol.	In case of pure $\text{Al}_2\text{O}_3$ catalyst the xerogel is 18 times more active than aerogel; the precipitated oxide is more active than the xerogel; pure $\text{Al}_2\text{O}_3$ is 2.6 times more active than a mixed catalyst, such as 9.4% $\text{Cr}_2\text{O}_3$ + 90.6% $\text{Al}_2\text{O}_3$ ; the aerogel of the mixed catalyst is twice as active as the xerogel; the xerogel acts more strongly in dehydrogenation.	Kearby: <i>Chem. Age (London)</i> , <b>37</b> , 427-428, (1937).
Dehydration of alcohol proceeds according to the derived equation: (Refer to C. 1937 I 2089) $dm/dt = K_1(M - m)/M$ , where $M$ is the number of mols of the substance entering into reaction in a time unit; $m$ , the number of mols of initial substance which did react; the ratio of the adsorption coefficient of water to that of alcohol by hydration at $350^\circ$ is 0.65; dehydration of both isomeric propyl alcohols proceeds according to the same equation as that of ethyl alcohol; the relative adsorption coefficient of water to that of $n$ -propyl and isopropyl alcohol corresponds to the ratio of ethyl alcohol dehydration; the equality of the relative adsorption coefficient is ascribed to the equal orientation of molecules of homologous alcohols to the catalyst surface.	$\text{Al}_2\text{O}_3$ (Kahlbaum).	Bork and Tolstopjatowa: <i>Acta Physicochim. U.R.S.S.</i> , <b>8</b> , 577-590 (1938); <b>8</b> , 591-602 (1938); Refer also to Bork and Tolstopjatowa: <i>Ibid.</i> , <b>8</b> , 603-616 (1938).

Table 3. Joint Catalytic Dehydration of Alcohol and Ammonia or Aniline.

Reaction	Catalyst	Observer
Joint dehydration of $\text{C}_2\text{H}_5\text{OH}$ and $\text{NH}_3$ or aniline to alkyl amines.	Th and Al oxides.	Sabatier and Mailhe: <i>Compt. rend.</i> , <b>148</b> , 898 (1909); <b>150</b> , 823 (1910).
Dehydration of $\text{CH}_3\text{OH}$ and $n$ -butyl alcohols plus $\text{NH}_3$ .	CeO on pumice, alumina on pumice, silica gel + NiO (prepared at $465^\circ$ ) most active, silica gel + ThO <sub>2</sub> .	Brown and Reid: <i>J. Phys. Chem.</i> , <b>28</b> , 1067 (1924).

Table 3 (Continued).

Reaction	Catalyst	Observer
Joint dehydration of $C_2H_5OH$ plus $NH_3$ or aniline.	$Al_2O_3$ .	Dorrell: <i>J. Chem. Soc.</i> , <b>127</b> , 2399 (1925).
Dehydration of $C_2H_5OH$ plus $NH_3$ .	Alumina, Th-silica gel, kaolin and blue W oxide.	Briner and Gemdillon: <i>Helv. Chim. Acta</i> , <b>14</b> , 1283 (1931).
Dehydration of alcohol plus $NH_3$ .	90% $Al_2O_3$ + 10% $Fe_2O_3$ .	Shujkin, Balandin and Plotkin: <i>J. Phys. Chem.</i> , <b>39</b> , 1207 (1935).
Dehydration of alcohol plus $NH_3$ ; T. 360–400°.	(1) Alumina (2) $Al_2O_3$ (90%) + $Fe_2O_3$ (10%) (3) $Al_2O_3$ (80%) + $Cr_2O_3$ (20%) (4) $Al_2O_3$ (90%) + $SnO$ (10%) (5) $Al_2O_3$ (90%) + $ZnO$ (10%) Sequence of decreasing activity: $Al_2O_3 + Cr_2O_3 > Al_2O_3 + SnO > Al_2O_3 + Zn > Al_2O_3 > Al_2O_3 + Fe_2O_3$ ; mixed catalysts except 90% $Al_2O_3$ + 10% $Fe_2O_3$ at 360° and 400° when compared to pure alumina decrease the reaction rate in formation of amines from $C_2H_5OH$ and $NH_3$ ; advantage of 90% $Al_2O_3$ and 10% $Fe_2O_3$ over pure alumina consists in smaller decomposition of the alcohol; the action of mixed catalyst is not additive.	Shujkin, Balandin and Plotkin: <i>J. Phys. Chem.</i> , <b>39</b> , 1197 (1935).
Dehydration of alcohol: aniline (1:1.45).	Pure alumina + oxides of metals used for dehydrogenation.	Shujkin, Balandin and Dimov: <i>J. Phys. Chem.</i> , <b>39</b> , 1207 (1935).
Dehydration of o-amino phenylethyl alcohol to o-amino styrol (heated in vacuum) and o-amino phenylethyl alcohol to indoline with small amount of indol and o-amino styrol; T. 250–400°.	$K_2CO_3$ anhydrous. $Al_2O_3$ , $TiO_2$ , $ZrO_2$ , bauxite, silicic acid and hydrosilicate.	I. G. Farbenindustrie A.-G. (Breuers): G.P. 606,027 (1934).

Table 4. Catalytic Dehydration of Alcohol to Ether.

Reaction	Catalyst	Observer
Dehydration of alcohol to ether formation: $2C_2H_5OH \rightleftharpoons C_2H_5OC_2H_5 + H_2O$ ; T. 250–300°; condensation under elevated pressure; T. 250°, ether formation after 1 hr., 82.2% and 73.5%.	$Al_2O_3$ , $ThO_2$ , $WO_3$ .  $Al_2O_3$ .	Pease and Young: <i>J. Am. Chem. Soc.</i> , <b>46</b> , 390 (1924). Yatkar and Watson: <i>J. Soc. Chem. Ind.</i> <b>45T</b> , 168 (1928).
Dehydration of ethyl alcohol at temperatures below those at which formation of ethylene hydrocarbons takes place.	Kaolin, Al silicate.	Skärblom: Swed. P. 60,916 (Refer to C. 1928 I 1709).
Dehydration of alcohol T. 250°; ether yield, 70.5–74.3%.	$Al_2O_3$ (precipitated from Na aluminate solution by heating to 350–400°).	Clark, Graham and Winter: <i>J. Am. Chem. Soc.</i> , <b>47</b> , 2748 (1925).
Dehydration of primary alcohols of the fatty series to ether at low temp.; at high temp., dehydration proceeds to the formation of unsaturated hydrocarbons.	Japanese acid earth.	Inoue: <i>Bull. Chem. Soc. Japan</i> , <b>1</b> , 197 (1926). Kashima: <i>Bull. Chem. Soc. Japan</i> , <b>4</b> , 177 (1929).
Dehydration of alcohol T. 354°; after 25 min. maximum ether yield 55%; T. 269° and 300°; after 1 hr., 82.2% and 73.5%.	$Al_2O_3$ (precipitate of a dilute Al nitrate solution with $NH_3$ , dried 18 hrs. at 240–250°.	Alvarado: <i>J. Am. Chem. Soc.</i> , <b>50</b> , 790 (1928).
Dehydration of ethyl alcohol; T. 150–200° to diethyl ether.	Active bleaching earth.	Rheinische Kampfer Fabrik: G.P. 638,756 (1936). F.P. 681,049 (1930).

Table 5. Catalytic Dehydration of Alcohols.

Reaction	Catalyst	Observer
Dehydration of alcohol.	Glowed clay, silicic acid.	Deimann, van Troostwyk, Bondt and Lauwrenbrough: <i>Crell's Chem. Ann.</i> (2), 312, 438 (1795).
Higher alcohols prepared by heating lower alcohols.	Alkali.	Guerbet: <i>Compt. rend.</i> , 128, 511 (1901); 132, 207 (1901); 133, 1220 (1901); 135, 171 (1902); <i>Ann. chim.</i> , 27 (7) 67, 105 (1902).
Dehydration of polyatomic alcohols, e.g., ethylene glycol, to form ethylene oxide which isomerizes into acetaldehyde.	Alumina.	Ipatieff and Leontovitch: <i>J. Russ Phys.-Chem. Soc.</i> , 35, 606 (1903)
(1) $\text{CH}_2\text{OH}-\text{CH}_2\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3-\text{CHO}$		
(2) $\text{CH}_3-\text{CH}_2-\text{O} \rightarrow \text{CH}_3-\text{C}(=\text{O})-\text{H}$		
Dehydration of mono- and polyunsaturated, saturated, and cyclic alcohols.	$\text{Al}_2\text{O}_3$ .	Ipatieff: <i>J. Russ. Phys.-Chem. Soc.</i> , 36, 813 (1904).
(1) $2\text{R} \cdot \text{OH} \rightarrow \text{H}_2\text{O} + \text{R} \cdot \text{OR}$ (ether)		
(2) $2\text{C}_n\text{H}_{2n+1}\text{OH} \rightarrow 2\text{H}_2\text{O} + 2\text{C}_n\text{H}_{2n}$ (ethylene hydrocarbon)		
Dehydration of alcohol.	$\text{Al}_2\text{O}_3$ (Na salts decrease activity).	Senderens: <i>Compt. rend.</i> , 146, 125 (1909).
Dehydration of bivalent alcohols to diolefins; pinacone to methyl isoprene (70%); T. 400°.	$\text{Al}_2\text{O}_3$ .	Badische Anilin- und Soda-Fabrik: F.P. 417,275 (1910).
Dehydration of unsaturated alcohols to diolefins; T. 380-400°; diminished pressure.	Al silicate and $\text{Al}_2\text{O}_3$ .	Kyriakides: <i>J. Am. Chem. Soc.</i> , 36, 980 (1914).
Butene (2)-ol-(1) → butadiene.		
Pentene (2)-ol-(4) → piperylene.		
Dehydration of allyl alcohol; T. 350°.	$\text{WO}_3$ .	Sabatier and Kubota: <i>Compt. rend.</i> , 173, 17 (1921).
Dehydration of alcohols to olefins; T. 300-326°; yield, 96.6% ethylene.	Equal parts of pumice and $\text{Al}_2\text{O}_3$ .	Goris: <i>Chimie &amp; industrie</i> , 11, 125T, 449 (1924).
Dehydration of alcohol; T. 250°; maximum ether yield 60%.	$\text{Al}_2\text{O}_3$ (glowing in alkali or $\text{H}_2\text{SO}_4$ causes $\text{Al}_2\text{O}_3$ to lose solubility and dehydration ability).	Pease and Jung: <i>J. Am. Chem. Soc.</i> , 46, 390 (1924).
Dehydration of alcohol.	$\text{Al}_2\text{O}_3$ (precipitated from Na aluminate).	Senderens: <i>Bull. soc. chim.</i> (4), 35, 1144 (1924).
Dehydration of alcohols.	Small size of pores very important factor in the case of $\text{Al}_2\text{O}_3$ catalyst; $\text{Al}_2\text{O}_3$ prepared from aluminum amalgam and water is doubly active in comparison with that prepared from aluminum isopropylate on pumice.	Adkins: <i>J. Am. Chem. Soc.</i> , 44, 2176 (1922). Adkins and Nissen: <i>J. Am. Chem. Soc.</i> , 46, 130 (1924).
Dehydration of alcohols to olefins; their formation is a linear function of temp. if conditions for catalyst are maintained.	(1) Small amount of $\text{Al}_2\text{O}_3$ . (2) Same temp. all over. (3) Double amount of alcohol passed with respect to that dehydrated.	Adkins and Perkins: <i>J. Am. Chem. Soc.</i> , 47, 1163 (1925).
Dehydration of alcohols at high temp. to olefins.	$\text{Al}_2\text{O}_3$ + small amts. of oxides of heavy metals from 1st, 6th, 7th, or 8th group Periodic System (CuO, CuO + Ag <sub>2</sub> O, Cr <sub>2</sub> O <sub>3</sub> , NiO).	I. G. Farbenindustrie A.-G.: E.P. 313,426 (1929).
Dehydration of alcohols.	$\text{Al}_2\text{O}_3$ (prepared from Na aluminate by precipitating with HCl or from Al sulfate precipitated with $\text{NH}_3$ ).	Alexejewskii and Preyss: <i>Zhur. Priklad. Khimii</i> , 3, 859 (1930).
Intermolecular dehydration of two lower alcohol molecules to form higher alcohols.		Graves: <i>Ind. Eng. Chem.</i> , 23, 1381 (1931).



Table 5 (Continued).

Reaction	Catalyst	Observer
Dehydration to form higher alcohols by the following reactions: (1) $\text{CH}_3\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{OH}$ (hydrogen atom attached either to the C atom of methane or to the $\beta$ -carbon atom). (2) $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (3) $\text{CH}_3\text{OH} + \text{HCH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (4) $\text{CH}_3\text{OH} + \text{CH}_3\text{HCHCH}_2\text{OH} \rightarrow \text{CH}_3\text{CHCH}_2\text{CH}_2\text{OH}$ (secondary alcohols are supposed to be formed also by a dehydration involving an H atom attached to the C atom holding the OH group).		
Dehydration of alcohol.	$\text{Al}_2\text{O}_3$ (maximum activity; age of contact, between 42-64 days (from date of preparation).	Huttig and Brull: <i>Ber.</i> , <b>65</b> , 1795 (1932).
Dehydration of secondary alcohols to olefins (high temp.).	$\text{Al}_2\text{O}_3$ .	Dupont (Taylor and Lazier): U.S.P. 1,895,529 (1933).
Dehydration of alcohol.	$\text{Al}_2\text{O}_3$ (optimum activity when $\text{H}_2\text{O}$ content is 5.5%).	Munro and Horn: <i>Can. J. Res.</i> , <b>12</b> , 707 (1935).
Dehydration of alcohols; T. 180-300°.	$\text{H}_3\text{PO}_4$ precipitated on silicic acid or kieselguhr contact.	Universal Oil Products Co. (Ipatieff): U.S.P. 2,018,065 (1935).

Table 6. Catalytic Dehydration of Propyl and Isopropyl Alcohol.

Reaction	Catalyst	Observer
Dehydration of propyl and isopropyl alcohol to propylene. $2\text{C}_3\text{H}_7\text{OH} + \text{Al}_2\text{O}_3 \rightarrow 2\text{AlO} \cdot \text{O} \cdot \text{C}_3\text{H}_7 + \text{H}_2\text{O}$ $2\text{AlO} \cdot \text{O} \cdot \text{C}_3\text{H}_7 + 2\text{C}_3\text{H}_7\text{OH} \rightarrow 2(\text{C}_3\text{H}_7)_2\text{O} + 2\text{AlOOH}$ $2\text{AlOOC}_3\text{H}_7 \rightarrow 2\text{C}_3\text{H}_6 + 2\text{AlOOH}$ with increasing temp. the reaction is shifted toward propylene formation; starting with T. 250° the olefin splitting of alcohol is a monomolecular process; the ether formation is a bimolecular process; maximum temp. 360-400°.	$\text{Al}_2\text{O}_3$ contact highly heated.	Trautz and Winkler: <i>J. prakt. Chem.</i> , <b>104</b> , 44 (1922).
Dehydration of propyl alcohol to propylene; T. 360-370°.	$\text{Al}_2\text{O}_3$ .	Bonham: <i>J. Am. Pharm. Assoc.</i> , <b>14</b> , 114 (1925).
Dehydration of butyl alcohol to butylene; T. 480°.		Briner: <i>Helv. Phys. Acta</i> , <b>7</b> , 374 (1924).
Dehydration of isopropyl alcohol to 94% of propylene; T. 360°.	Tertiary Ca phosphate.	Allardyce: <i>Trans. Roy. Soc. Can.</i> , <b>21</b> , 315 (1927).
Conversion of primary propyl alcohol to hydrocarbons with two double bonds; methyl-2-pentadiene-1,3; T. 400°; yield 6% of the starting material.	Mixed catalyst.	Gorin and Neumark: <i>Zhur. Obshchei Khimii</i> , <b>5</b> (67) 1772-80 (1935).

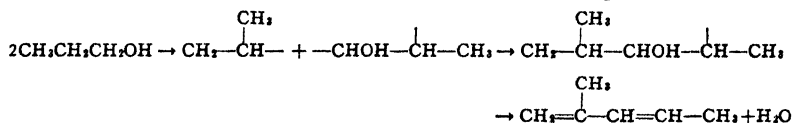


Table 7. Catalytic Dehydration of Butyl and Isobutyl Alcohol.

Reaction	Catalyst	Observer
Dehydration of butyl alcohol.	$\text{Al}_2\text{O}_3 + 90\% \text{H}_3\text{PO}_4$ .	Faworski (1890).
Dehydration of butyl alcohol; T. 250-300°.	$\text{Na}_2\text{PO}_3 + \text{bauxite}$ .	I. G. Farbenindustrie A.-G.: F.P. 679,998, E.P. 367,892, March 24, 1932.

Table 7 (Continued).

Reaction	Catalyst	Observer
Dehydration of butyl alcohol to isobutene. (a) T. 250°. (b) T. 350-400°.	90% $\text{H}_3\text{PO}_4$ impregnated at 190°. (a) on $\text{Al}_2\text{O}_3$ . (b) on pumice stone.	Komarewsky, Johnstone and Joder: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 2705-07 (1934).
Dehydration of butyl alcohol.	$\text{H}_3\text{PO}_4$ , $\text{Na}_2\text{HPO}_4$ , $\text{MgH}_2(\text{PO}_4)_2$ .	
Dehydration of isobutanol. (1) normal dehydration: water removed from adjacent C atoms $(\text{CH}_3)_2\text{CHCH}_2\text{OH} \rightarrow \text{H}_2\text{O} + (\text{CH}_3)_2\text{C}=\text{CH}_2$ (open chain olefin obtained). (2) abnormal dehydration: the hydroxyl group and H atom come from non-adjacent C atoms $(\text{CH}_3)_2\text{CHCH}_2\text{OH} \rightarrow$ $\text{H}_2\text{O} + (\text{CH}_3)\text{CH} \begin{array}{l} \text{CH}_2 \\ \text{CH}_2 \end{array}$ (a closed chain olefin obtained).	$\text{ZnCl}_2$ .	Ipatieff: "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Co., New York, 1936.

Table 8. Catalytic Dehydration of Amyl and Isoamyl Alcohol.

Reaction	Catalyst	Observer
Dehydration of isoamyl alcohol; T. 250°.	Alumina + various additions.	Ipatieff: <i>J. Soc. Chem. Ind.</i> , <b>32</b> , 638 (1913).
Dehydration of fermentation amyl alcohol to amylene; T. 340-350°.	Al silicate.	Senderens: <i>Compt. rend.</i> , <b>171</b> , 916 (1920).
Dehydration of amyl alcohol to amylene.	$\text{Al}_2\text{O}_3$ activated by addition of a small amount of oxides of heavy metals of the 1st, 6th, 7th and 8th group.	I. G. Farbenindustrie A.-G.: E.P. 313,426 (1929).
Dehydration of isoamyl alcohol.	$\text{Na}_2\text{HPO}_4$ + red P. $\text{NaH}_2\text{PO}_4$ + $\text{Al}(\text{OH})_3$ .	I. G. Farbenindustrie A.-G.: E.P. 367,892, March 24, 1932.

Table 9. Catalytic Dehydration of Glycols.

Reaction	Catalyst	Observer
Dehydration of ethylene glycol to acetaldehyde and water; dehydration of pinacol to pinacolone; T. 300-320°.	$\text{Al}_2\text{O}_3$ .	Ipatieff and Leontovitch: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>35</b> , 606 (1903).
Dehydration of butylene glycol to diolefin; polymerized to a rubbery mass; 2-methylbutanediol-1,3 gives analogous isoprene and 2,4-pentandiol piperylene; T. 380-400°.	Kaolin.	Kyriakides: <i>J. Am. Chem. Soc.</i> , <b>36</b> , 980 (1914).
Dehydration of butylene glycol to erythrene at 350-480° and isoamylene glycol to isoprene at 400-450°.	$\text{Al}_2\text{O}_3$ .	Ostromyslenski: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>47</b> , 1472, 1947 (1915).
Dehydration of glycerin to acrolein + $\text{H}_2\text{O}$ to ethylene + CO; decomposed to higher aldehydes and condensed with $\text{H}_2\text{O}$ to acrolein; T. 180°.	$\text{Al}_2\text{O}_3$ ; 25% kieselguhr, bleaching earth chemically active.	Sabatier and Gaudion: <i>Compt. rend.</i> , <b>166</b> , 1034 (1918). Shering and Freund Chemische Fabrik: G.P. 451,535 (1927).
Dehydration of divinyl glycol to cyclic aldehyde, 1-methylcyclopentene-1; 60% yield; T. 280°.	$\text{Al}_2\text{O}_3$ .	Urion: <i>Compt. rend.</i> , <b>190</b> , 1512 (1930).
Dehydration of 1,3-butylene glycol to butadiene.	100 p. Monophosphate precipitated on graphite or coke.	I. G. Farbenindustrie A.-G.: E.P. 326,185 (1930).
Dehydration of glycol to butadiene and isoprene.	$\text{H}_3\text{PO}_4$ or its acid salts: $\text{NaH}_2\text{PO}_4$ , $\text{MgH}_2(\text{PO}_4)_2$ ; sulfates and $\text{Al}_2(\text{SO}_4)_3$ .	I. G. Farbenindustrie A.-G.: E.P. 326,185 (1930). E.P. 698,426 (1931). F.P. 686,446 (1930).

Table 9 (Continued).

Reaction	Catalyst	Observer
Dehydration of glycols to ketones; 1,3-butylene glycol to methyl ethyl ketone; 70% yield; T. 220°.	Heavy metals of the 1st and 8th groups and oxides, hydroxides, oxalates, formates of elements of an alkaline character on carriers: fuller's earth, silicic acid, or added activating substances, such as $\text{Al}_2\text{O}_3$ (colloidal silicic acid may be added); 100 p. $\text{CuO}$ , 35 p. $\text{Al}_2\text{O}_3$ and 100 p. of 1.5% solution of colloidal silicic acid on Al particles.	I. G. Farbenindustrie A.-G.: (Reppe): G.P. 510,712 (1930). G.P. 528,360 (1931).
Dehydration of 1,3-butylene glycol to butanols (unsaturated alcohols).	Mixture of metal oxides, 5th to 7th groups, on kieselguhr or $\text{Al}_2\text{O}_3$ .	I. G. Farbenindustrie A.-G.: (Runge): G.P. 536,362 (1931).
Dehydration of tertiary alcohols.	Kieselguhr, fuller's earth, active charcoal, besides $\text{Al}_2\text{O}_3$ .	Hercules Powder Co. (Humphrey): U.S.P. 1,893,802 (1932).
Dehydration of higher polyvalent alcohols to high molecular unsaturated hydrocarbons.	Bauxite, $\text{Al}_2\text{O}_3$ .	I. G. Farbenindustrie A.-G.: G.P. 583,564 (1933).
Dehydration of glycol monoethyl ether to butadiene; T. 230–450°.	$\text{Al}_2\text{O}_3$ (calcination of ammonia alum).	Chalmers: G.P. 599,503 (1934).
Dehydration of 1,3-butylene glycol to butadiene; T. 180–300°.	$\text{H}_3\text{PO}_4$ on silica gel or kieselguhr.	Ipatieff: U.S.P. 2,018,065 (1935).

Table 10. Catalytic Dehydration of Carbinols.

Reaction	Catalyst	Observer
Dehydration of phenyl benzyl carbinol: $\text{C}_6\text{H}_5\text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{CH} : \text{CH} \cdot \text{C}_6\text{H}_5$ to unsaturated hydrocarbons and methyl phenyl carbinol to styrol.	$\text{Al}_2\text{O}_3$ . (If $\text{H}_3\text{PO}_4$ is used, styrol is at once polymerized to metastyrol) (with sulfonic acids the chief product is the corresponding ether and a small amount of styrol).	Sabatier and Murat: <i>Ann. chim.</i> (9), 4, 284 (1915).
Dehydration of isobutyl carbinol.	40% infusorial earth, 30% ton and 30% cork flour mixed with water, dried, and heated up to 900–1000°.	Puyal: <i>Anales soc. espan. fis. quim.</i> , 20, 81–83 (1922).
Dehydration of cyclic paraffinic alcohols: cyclopropyl carbinol, cyclobutanol to erythrene; methylcyclobutanol to isoprene; methylcyclopropylcarbinol to piperylene (together with dehydration a ring splitting or rearrangement takes place).	$\text{Al}_2\text{O}_3$ .	Dojarenko: <i>J. Russ. Phys.-Chem. Soc.</i> , 58, 16, 27 (1926).
Dehydration of fatty aromatic alcohols to cyclic hydrocarbons, e.g., diphenylmethyl carbinol to 9-methylfluorene; T. 300°; pretreated with $\text{H}_2$ at 180°.	Pt-charcoal contact.	Zelinsky and Gawerdowskaja: <i>Ber.</i> , 61, 1049 (1928).
Dehydration of methyl phenyl carbinol to styrol; T. 290–300° yield, 90% styrol.	$\text{Al}_2\text{O}_3$ precipitated together with pumice.	I. G. Farbenindustrie A.-G. (Laage): G.P. 533,827 (1931).
Dehydration of diethyl carbinol to olefins at high pressures; T. 365–410°.	$\text{H}_3\text{PO}_4$ on silica gel.	Karnatz and Whitmore: <i>J. Am. Chem. Soc.</i> , 54, 3461 (1932).
Dehydration of methyl vinyl carbinol to erythrene (25%) and ethyl vinyl carbinol to pentadiene (60–70%) at 350–365°; dehydration of propyl vinyl carbinol to hexadiene and butyl vinyl carbinol to heptadiene at 250–280°.	$\text{Al}_2\text{O}_3$ . $\text{Al}_2\text{O}_3$ obtained from Na aluminate by precipitating with $\text{CO}_2$ . $\text{Al}_2\text{O}_3$ mixed with pumice.	Lespieu and Prévost: <i>Bull. soc. chim.</i> (4), 34, 710 (1934). Prévost: <i>Compt. rend.</i> , 182, 853 (1926). Dumoulin: <i>Compt. rend.</i> , 182, 974 (1926).
Dehydration of dimethylcyclobutyl carbinol in 2 directions:	Dehydrating catalysts.	Kasansky: <i>Ber.</i> , 69, 950–54 (1936).

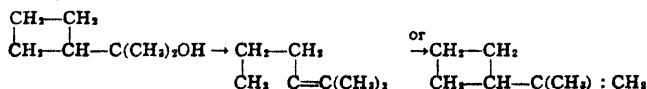


Table 11. Catalytic Dehydration of Hydroaromatic Alcohols.

Reaction	Catalyst	Observer
Dehydration of cyclohexanol to cyclohexene; T. 350°.	Al <sub>2</sub> O <sub>3</sub> .	Ipatieff: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>38</b> , 92 (1906).
Dehydration of o-methylcyclohexanol to methylcyclohexene; T. 350° and decahydronaphthalene to octahydronaphthalene.	Al <sub>2</sub> O <sub>3</sub> .	Ipatieff: <i>Ber.</i> , <b>43</b> , 3383 (1910).
Dehydration of dimethylcyclohexanol.	Alumina.	Senderens: <i>Ann. chim.</i> (8), <b>25</b> , 501 (1912).
Dehydration of cyclohexanol to cyclohexene at 200° in the presence of air or CO <sub>2</sub> .	Japanese acid earth.	Inoue: <i>Bull. Chem. Soc. Japan</i> , <b>1</b> , 219 (1926).
Dehydration of cyclohexanol to cyclohexene (1/2 hr. boiling).	Kieselguhr, 10% chemically active bleaching earth (silica gel, non-active).	Shering and Freund Chemische Fabrik: G.P. 451,535 (1927).
Dehydration of cyclohexanol to cyclohexene; T. 250–300°.	Activated birchwood, ZnCl <sub>2</sub> -charcoal.	Bahr: <i>Ber.</i> , <b>64</b> , 2258 (1931).

Table 12. Catalytic Dehydration of Cyclic and Bicyclic Terpene Alcohols.

Reaction	Catalyst	Observer
Dehydration of cyclic and bicyclic terpene alcohols; borneol to camphene at 350°, menthol to menthene at 370° and borneol to camphene at 220°.	Al <sub>2</sub> O <sub>3</sub> (kieselguhr, bleaching earth, silica gel, active charcoal), Al <sub>2</sub> O <sub>3</sub> +CuO (small amounts).	Ipatieff: <i>Ber.</i> , <b>45</b> , 2035 (1912). Ipatieff and Rutala: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>44</b> , 1692 (1912).
Dehydration of olefinic and cyclic terpene alcohols to terpene hydrocarbons; l-linalool to olefinic terpene myrcene+isomeric cyclic terpene d-limonene; terpineol at 159° to dipentene; d-borneol at 200° to camphene.	10% Japanese acid earth.	Ono and Takeda: <i>Bull. Chem. Soc. Japan</i> , <b>2</b> , 16 (1927). Ono: <i>Ibid.</i> , <b>1</b> , 248 (1926).
Dehydration of borneol to camphene.	5% by weight chemically active bleaching earth.	Shering and Freund Chemische Fabrik: G.P. 451,535 (1927).
Dehydration of cetyl alcohol to hexadecylene; T. 340–350°.	Al <sub>2</sub> O <sub>3</sub> .	Sandonnini and Bezzi: <i>Atti accad. Lincei</i> (6), <b>12</b> , 154 (1930).
Dehydration of 100 p. 8-menthol to 85 p. 3-menthene at 300°.	Activated bleaching earth.	Schering-Kahlbaum A.-G. (Schoeller and Borgwandt): G.P. 569,689 (1933). (F.P. 713,357 1931). E.P. 370,288 (1932).
Dehydration of borneol and isoborneol (+3–4% toluene) to camphor; yield almost quantitative.	Cu carbonate (1–2%) (obtained from CuSO <sub>4</sub> and Na <sub>2</sub> CO <sub>3</sub> ).	Salkind, Michelis and Stojalow: <i>Russ. P.</i> 42,076, March 31, 1935.
Dehydration of fenchyl alcohol to fenchene+some other kind of terpene.	Kaolin or florida earth.	Toivonen, Veijola and Friberg: <i>Acta Chem. Fennica</i> , <b>8</b> , 44B (1935).
Dehydration of terpene alcohols; 200 g. geraniol to 130 g. of oil containing myrcene and dipentene at 225°.	Kieselguhr and active charcoal (40 g.).	Kimura: <i>Bull. Chem. Soc. Japan</i> , <b>10</b> , 330 (1935).
Dehydration of 100 g. α-terpineol to dipentene; 5 hrs., T. 200°; yield 67.9 g.; oily product; and 1-menthol to 3-menthene; T. 200°; yield 62.8% oil.	20 g. Active charcoal.  20% Active charcoal.	Kimura: <i>Ibid.</i> , <b>10</b> , 330 (1935).

Table 13. Catalytic Dehydration of Formic Acid.

Reaction	Catalyst	Observer
Dehydration of formic acid; 1 vol. formic acid added slowly to 6 vol. conc. H <sub>2</sub> SO <sub>4</sub> at 15°; at 40°, develops stormy gas.	H <sub>2</sub> SO <sub>4</sub> acts as a dehydrating agent and a catalyst; small amount of Al sulfate or K bisulfate will improve the action.	Senderens: <i>Compt. rend.</i> , <b>184</b> , 856 (1927).
Dehydration of formic acid to form 90% CO. T. 330° and 280–330°.	ThO <sub>2</sub> -SiO <sub>2</sub> (P <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub> ) (TiO <sub>2</sub> -SiO <sub>2</sub> ) + Al phosphate.	Graeber and Cryder: <i>Ind. Eng. Chem.</i> , <b>27</b> , 828–31 (1935).

Table 14. Catalytic Dehydration of Acetic Acid.

Reaction	Catalyst	Observer
Ketonization of acetic acid or dehydration of acetic acid to acetone.	Ba acetate impregnated on pumice.	Squibb: <i>J. Am. Chem. Soc.</i> , <b>17</b> , 187 (1895).
Dehydration of acetic acid to form acetone (splitting off water and carbon dioxide): $2\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2\text{O} + \text{CO}_2$ T. 340–400°; T. 250–280°; T. 400°.	ThO <sub>2</sub> , UO <sub>2</sub> . Zn dust. ZnO.	Sabatier, Senderens and Maihle: <i>Compt. rend.</i> , <b>146</b> , 1211 (1908); <b>148</b> , 927 (1909); <b>149</b> , 995 (1909); <b>154</b> , 1518 (1912); <b>156</b> , 830 (1913); <b>156</b> , 1730 (1913); <b>157</b> , 219 (1913). Senderens: <i>Bull. soc. chim.</i> , <b>3</b> , 824 (1908). <i>Ann. chim.</i> , <b>4</b> , 476 (1905); <b>5</b> , 905 (1909); <b>5</b> , 916 (1909). Maihle: <i>Bull. soc. chim.</i> , <b>5</b> , 618 (1909). <i>Chem. Ztg.</i> , <b>33</b> , 242, 253 (1909).
Dehydration of acetic acid and benzoic acid to acetophenone and CO <sub>2</sub> ; T. 400–500°; 1.5 parts acetic acid and 1.0 part benzoic acid. $\text{C}_6\text{H}_5\text{COOH} + \text{H} \cdot \text{OOC} \cdot \text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{COCH}_3 + \text{H}_2\text{O} + \text{CO}_2$ T. 550°; yields 80% acetophenone.	Fe <sub>2</sub> O <sub>3</sub> (obtained by glowing Fe oxalate eliminating air); Mn oxydule obtained by heating Mn carbonate in CH <sub>3</sub> OH vapor.  ThO <sub>2</sub> precipitated on pumice.	Sabatier and Maihle: <i>Compt. rend.</i> , <b>159</b> , 217 (1914).
Dehydration of acetic acid; T. 350°.	Active Fe, MnO.	Union Carbide Co.: U.S.P. 1,315,525 (1919).
Dehydration of acetic acid; T. 300–400°.	Granulated Al.	Stockholm Superfosfate Fabriks Aktiebolaget: E.P. 171,391 (1921). Swed. P. 53,894 (1922); (Refer to C. 1923 IV 945). F.P. 543,283 (1922).
Dehydration of acetic acid; T. 350–450°.	Th compounds.	Elektrizitätswerke Lanza: Swiss P. 102,276 (1923). E.P. 192,392 (1922). F.P. 561,377 (1923).
Dehydration of acetic acid; T. 600–700° (temp. dropped to 15–20°). $2\text{CH}_3\text{COOH} \rightleftharpoons (\text{CH}_3\text{CO})_2\text{O} + \text{H}_2\text{O}$	Na metaphosphate or melts from Li carbonate and Na metaphosphate.	Konsortium für Elektrochemische Industrie: G.P. 410,363 (1925). G.P. 417,731 (1925). E.P. 194,719 (1923). E.P. 230,063 (1924). E.P. 272,923 (1927). E.P. 272,951 (1927). Swiss P. 101,168 (1923). F.P. 634,466 (1927). F.P. 563,452 (1923). Can. P. 243,849, Oct. 21, 1914.
Dehydration of acetic acid anhydride at 635° to ketene. $(\text{CH}_3\text{CO})_2\text{O} \rightleftharpoons 2\text{CH}_2 = \text{CO} + \text{H}_2\text{O}$	Al sulfate.	Ketoid Co.: E.P. 237,573 (1925).
Dehydration of acetic acid; T. 250°.	H <sub>3</sub> PO <sub>4</sub> (pumice pieces added).	Dreyfus: E.P. 280,972 (1927).
Dehydration of acetic acid to anhydride; T. 200–700°.	H <sub>3</sub> PO <sub>4</sub> impregnated on kieselguhr.	Dreyfus: E.P. 312,733 (1929).
Dehydration of acetic acid to acetic anhydride (extensively used in synthetic processes).	Silicon carbide impregnated with H <sub>3</sub> PO <sub>4</sub> (tube made of Pt or Au).	Dreyfus: E.P. 312,733 (1929).
Dehydration of acetic acid diluted with N <sub>2</sub> , CO <sub>2</sub> or benzene; T. 400–800°.	Quartz, Cu, graphite or Au tube filled with activated charcoal.	British Celanese Company: E.P. 312,587 (1929).
Dehydration of acetic acid to acetic anhydride; temp. 600–700° (the vapors are cooled as fast as possible to 15–20°).	Na metaphosphate, alkaline-earth phosphate, activated coal, Cu, graphite or Au tube.	British Celanese Company: E.P. 312,587 (1929).
Dehydration of acids to anhydrides; acetic acid to acetic anhydride.	Al <sub>2</sub> O <sub>3</sub> .	Boehringer und Söhne G.m.b.H. (Müller, Hatzig and Rabald): G.P. 566,332 (1932).

Table 14 (Continued).

Reaction	Catalyst	Observer
Dehydration of acetic acid to acetic anhydride (the acetic acid vapors are passed through melted boric anhydride); T. 850-1000°; *use high pressure and temp.	Al <sub>2</sub> O <sub>3</sub> .	Courtaulds, Ltd. (Brown): E.P. 369,710 (1932). E.P. 383,727 (1932). *Campardon and Folie-Desjardins: P.P. 683,815 (1930).
Dehydration of acetic acid to acetic anhydride; temp. 700°; yield 53% of theoretical; yield up to 50%.	Silica gel (obtained by treating natural silicates, lenzinite and analcite with acids); this silicic acid skeleton (free from Fe and Mn) may be charged with Pt or charcoal serving then as carrier.	Boehringer und Söhne G.m.b.H. (Müller and Hatzig): G.P. 603,234 (1934); Refer also to E.P. 369,283 (1932).

Table 15. Catalytic Dehydration of Acids.

Reaction	Catalyst	Observer
Dehydration of acids, such as low molecular weight fatty acids, to anhydrides; T. up to 800°.	Charcoal, alumina.	Konsortium für Elektrochemische Industrie: (Meingast and Mugdan): G.P. 408,715 (1925).
Dehydration of maleic acid and tetrahydroquinoline cyclohexyl phenol.	Pd. Pd wire gauze covered with electrolytic Pd.	Akabori and Susuki: <i>Proc. Imp. Acad. (Tokyo)</i> , <b>5</b> , 255-256 (1930).

Table 16. Catalytic Dehydration of Ketones.

Reaction	Catalyst	Observer
Dehydration of bicyclic terpene ketones, and also of camphor to isocamphene; T. 200°.	NiO + Al <sub>2</sub> O <sub>3</sub> .	Ipatieff: <i>Ber.</i> , <b>45</b> , 3205 (1912).
Dehydration of oxyketones: dimethylacetone to unsaturated ketone alcohol; vacuum distillation under 16 mm. pressure.	Al <sub>2</sub> O <sub>3</sub> .	I. G. Farbenindustrie A.-G. (Fleming and von der Horst): G.P. 577,256 (1933).

Table 17. Catalytic Dehydration of Aldehydes.

Reaction	Catalyst	Observer
Dehydration of terpene aldehydes, e.g., citral to <i>p</i> -cymol; 200 g. citral require 40 g. active coal; T. 135°.	Active charcoal.	Kimura: <i>Bull. Chem. Soc. Japan</i> , <b>10</b> , 330 (1935).
Dehydration of aldoxime to the nitrile of isovaleric aldoxime to the nitrile of valeric acid, and oenanthaldoxime to the nitrile of heptilic acid. $RCH : N \cdot OH \rightarrow R \cdot CN + H_2O$	Al <sub>2</sub> O <sub>3</sub> . Acetic anhydride or acetyl chloride.	Maihle and de Godou: <i>Bull. soc. chim.</i> (4), <b>23</b> , 18 (1918).

Table 18. Catalytic Dehydration of Amides.

Reaction	Catalyst	Observer
Dehydration of acetamide to acetonitrile; T. 260°; yield. 68%.	Charcoal, graphite, Al <sub>2</sub> O <sub>3</sub> .	Bechners and Andrews: <i>J. Am. Chem. Soc.</i> , <b>38</b> , 2503 (1916).
Dehydration of formamide to hydrogen cyanide.	Al <sub>2</sub> O <sub>3</sub> in the form of Alundum (obtained by electric melting of bauxite).	Imperial Chemical Industries, Ltd. (Evans): E.P. 305,816 (1928).
Dehydration of amides to nitriles below 400° good yield.	Silicic acid gel.	Mitchell and Reid: <i>J. Am. Chem. Soc.</i> , <b>53</b> , 321 (1931).

Table 19. Catalytic Dehydration of Phenols.

Reaction	Catalyst	Observer
Dehydration of hexahydrophenol (high pressure).	Ni <sub>2</sub> O <sub>3</sub> .	Ipatieff: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>37</b> , (1905).
Dehydration of phenol to phenyl oxide; T. 450°.	Th.	Sabatier and Espil: <i>Bull. soc. chim.</i> (4), <b>15</b> , 228 (1914).
Dehydration of phenols to diphenyl ether; T. 350°; yield, 15% of theoretical value. $2C_6H_5OH \rightarrow C_6H_5O \cdot C_6H_5 + H_2O$	Activated bleaching earth.	Rheinische Kampfer Fabrik (Schölkopf): G.P. 530,736 (1931).
Dehydration of phenols.	Th.	Briner and Bron: <i>Helv. Chim. Acta</i> , <b>15</b> , 1234-1241 (1932).

Table 20. Catalytic Dehydration of Various Organic Compounds.

Reaction	Catalyst	Observer
Dehydration of diethyl ether to ethylene; T. 200°.	Al silicate; better $Al_2O_3$ (obtained by hydrolysis of Al amalgam is twice as active as one prepared from Al propylate precipitated on pumice).	Senderens: <i>Bull. soc. chim.</i> (4), 3, 827 (1908). Adkins and Nissen: <i>J. Am. Chem. Soc.</i> , 46, 130 (1924).
Dehydration of the ether of methyl butanol to isoprene.	$Al_2O_3$ , charged; $W_2O_5$ , especially active.	
Dehydration of esters.	$ZnCl_2$ .	Sabatier and Maible: <i>Bull. soc. chim.</i> (4), 11, 369 (1912).
Dehydration of organic compounds.	Infusorial earth.	Puyal: <i>Anales soc. espan. fis. quim.</i> , 20, 81-83 (1922).
Dehydration of cholesterol in benzene, toluene, or xylene to dicholesterol ether; T. 300°.	Floridin, bentonite, kieselguhr, bauxite (silica gel is not a dehydrating agent).	Bills and McDonald: <i>J. Biol. Chem.</i> , 67, 753 (1926); 68, 821 (1927); 72, 1 (1931).
Dehydration of primary amines of organic compounds; formic acid and <i>m</i> -toluidine to <i>m</i> -tolunitrile; T. 450° yield 40%; equivalent amounts of aniline and formic acid methyl ester to aniline benzonitrile.	Silica gel, active alumina, active charcoal. Charcoal.	I. G. Farbenindustrie A.-G.: (Nicodemus); G.P. 482,943 (1929).
Dehydration of organic compounds.	$H_3PO_4$ .	I. G. Farbenindustrie A.-G.: E.P. 326,185, April 3, 1930.
Dehydration of ethylene cyanhydride to acrylic acid nitrile; T. 260°.	Active charcoal or silica gel.	I. G. Farbenindustrie A.-G. (Finkelstein); G.P. 496,372 (1930).
Dehydration of organic compounds.	$Al_2O_3$ (heated as a hydroxide).	Taylor and Levin: <i>J. Am. Chem. Soc.</i> , 52, 1910-1918 (1930).
Dehydration of organic compounds.	Pt on asbestos.	I. G. Farbenindustrie A.-G.: E. P. 357,749, Oct. 22, 1931.
Dehydration of organic compounds.	$Na_2WO_4$ , $(NH_4)_2MoO_4$ (Kato-kaolin).	Ao: <i>J. Soc. Chem. Ind. Japan</i> , 35, 567B-568B (1932).
Dehydration of organic compounds.	Base exchangers containing V, Ni, Si.	Selden Research Engineering Corporation (Koetz): U.S.P. 1,941,557, Jan. 2, 1934.
Dehydration of organic compounds.	$ThO_2 + SiO_2$ .	Graeber and Cryder: <i>Ind. Eng. Chem.</i> , 27, 828-831 (1935).
Dehydration of organic compounds.	1-2% $CuCO_3$ (from $CuSO_4 + Na_2CO_3$ ).	Salkind, Michelis and Stojalow: Russ. P. 42,076, March 31, 1935.
Denydration of lactones or the corresponding $\gamma$ -oxy-acids (unsaturated acids) to cyclic ketones.	Al-Mg silicates (chemical activators and natural bleaching earths).	I. G. Farbenindustrie A.-G. (Weissenborn); G.P. 625,758 (1936).
$R \cdot CH_2 \cdot \underset{\text{O}}{\underset{ }{CH}} \cdot CH_2 \cdot CH_2 \cdot C : O \rightarrow R \cdot \underset{\text{O}}{\underset{ }{CH}} \cdot CH_2 \cdot CH : CH - C : O + H_2O$		
Dehydration of $\alpha$ -methylfuran with freshly distilled aniline, <i>o</i> - and <i>p</i> -toluidine in an $H_2$ stream to prepare 1,2-disubstituted pyrroles; T. 470°; yield 12%.	$Al_2O_3$ .	Jurjew: <i>Zhur. Obshchei Khim.</i> 8 (70), 116-19 (1938).
Intramolecular dehydration of aliphatic ether with $NH_3$ to secondary aliphatic amines; T. 200-400° (vapor mixture of ether and $NH_3$ ); diethyl ether and aniline; T. 370-375°; yield 74% diethyl aniline, 12% aniline, 1% monoethylaniline (ether as vapor led through aniline in the vicinity of its critical point and the mixture treated as above); the secondary amines are characterized by their picrates and hydrochlorides; the yields of secondary amines vary with temp. used and are in general smaller in the case of $ThO_2$ than with $Al_2O_3$ ; $n$ -propyl ether to dipropyl amine $n$ -butyl ether to dibutyl amine $n$ -amyl ether to diamyl amine diethyl ether to diethyl amine	$ThO_2$ (prepared by heating $Th(NO_3)_4$ to 150°); $Al_2O_3$ (prepared by several hours heating of $Al(OH)_3$ to 150°); $Al_2O_3$ . $ThO_2$ (poor catalyst).	Chatterjee, Sanyal and Goswami: <i>J. Indian Chem. Soc.</i> , 15° 399-401 (1938).

## PART VIII

## Catalytic Reduction in Inorganic and Organic Chemistry

Table 1. Catalytic Reduction of Various Inorganic Compounds.

Reaction	Catalyst	Observer
Reduction of chlorates to chlorides, nitrates to nitrites, ferric to ferrous salts (indigo blue to white); $\text{SO}_2$ to $\text{H}_2\text{S}$ ; $\text{As}_2\text{O}_4$ to As.	$\text{Pd}_2\text{H}_2$ .	Gladstone and Tribe: <i>Chem. News</i> , <b>37</b> , 68 (1878).
Reduction of $\text{SO}_2$ with $\text{C}_2\text{H}_2$ to S-containing hydrocarbons; T. $400^\circ$ using an excess of carbonic gas.	$\text{Al}_2\text{O}_3$ or bauxite catalyst with heavy metal compounds.	Rhenania Verein Chemische Fabriken (Stuer and Grob): G.P. 372,715 (1923)
Reduction of $\text{SO}_2$ to S; $2\text{SO}_2 + 4\text{CO} \rightleftharpoons 4\text{CO}_2 + \text{S}_2$ ; T. $400-800^\circ$ ; space velocity, 70-500.	Hard Nafoleschdinsk bauxite composed of 28.98% $\text{Fe}_2\text{O}_3$ 62.27% $\text{Al}_2\text{O}_3$ , or Earthy bauxite composed of 33.65% $\text{Fe}_2\text{O}_3$ 45.77% $\text{Al}_2\text{O}_3$	Paschewski and Tabunow: <i>Zhur. Khim. Prom.</i> , <b>12</b> , 480-483 (1935).
Reduction of $\text{SO}_2$ .	$\text{Al}(\text{OH})_3$ mixed with a fireproof carrier material (a solid combustible substance), and a sintering agent, e.g., $\text{Na}_2\text{SiO}_3$ , the mixture is molded, dried and sintered at a temp. at which a part of the water of crystallization in $\text{Al}(\text{OH})_3$ still remains.	Consolidated Mining and Smelting Co. of Canada (Lepsoe and Mills): U.S.P. 2,080,359, May 11, 1937.
Reduction of $\text{HNO}_3$ with $\text{FeCl}_2$ in HCl acid medium (industrial process).	Molybdic acid.	Hae and Natuka: <i>Collection Czechoslov. Chem. Commun.</i> , <b>1</b> , 521-527 (1929).
Reduction of $\text{K}_3\text{Fe}(\text{CN})_6$ (industrial process).	Bone charcoal in alkali solution; $\text{MnO}_2$ and fuller's earth; $\text{NiO}$ , $\text{Fe}_2\text{O}_3$ , $\text{PbO}_2$ and $\text{CuO}$ are inactive.	Johns and Weden: <i>Biochem. Z.</i> , <b>147</b> , 53 (1934); (Refer to C. 1934 II 3584).

Table 2. Catalytic Reduction of Carbon Monoxide.

Reaction	Catalyst	Observer
Reduction of CO to synthol; T. $410^\circ$ ; 75 atm. pressure.	Alkalized Fe contact.	Fischer and Tropsch: <i>Brennstoff-Chem.</i> , <b>5</b> , 201, 217 (1924).
Reduction of CO; high temp. and pressure.	Fe, Ni, or Co, also their compounds (Th or Cd may be added) (free from metal chlorides).	I. G. Farbenindustrie A.-G.: E.P. 300,294 (1928).
Reduction of CO.	Fe.	Kodama: <i>J. Chem. Soc. Japan</i> , <b>32</b> , 4B-5B (1928); <b>32</b> , 6B (1929). Kodama: <i>Sci. Papers Inst. Phys. Chem. Research (Tokyo)</i> , <b>14</b> , 169-183 (1930).
Reduction of CO.	$\text{BeO}$ , $\text{MgO}$ . $\text{ZnO} + \text{Co} - \text{Cu}$ .	Kodama: <i>J. Chem. Soc. Japan</i> , <b>33</b> , 60B (1930).
Reduction of CO.	Co, Cu, or $\text{ThO}_2$ .	Kodama: <i>Sci. Papers Inst. Phys. Chem. Research (Tokyo)</i> , <b>12</b> , 211-224 (1930).
Reduction of CO.	Ni on asbestos.	Fujimura: <i>Ibid.</i> , <b>17</b> , 11-15 and 16-21, 1931.
Reduction of CO.	Co—Cu—MgO on pumice (cane sugar a more satisfactory carrier because of better gas adsorption).	Fujimura: <i>J. Chem. Soc. Japan</i> , <b>34</b> , 384B (1931).
Reduction of CO at ordinary pressure.	Co—Cu—MgO=3 : 1 : 0.45 with additional substances.	Fujimura: <i>Ibid.</i> , <b>34</b> , 227B-229B (1931).
Reduction of CO.	Ni + dehydrating catalysts: $\text{ThO}_2$ , $\text{Al}_2\text{O}_3$ , $\text{SiO}_2$ , Cu, Mn, Cd, Zn, Pb.	Selden Co. (Jaeger): U.S.P. 1,824,896, Sept. 29, 1931.



Table 2 (Continued).

Reaction	Catalyst	Observer
Reduction of CO.	Special highly alloyed steel, containing Cr, W, Mo, V; advisable to use steel with a high Mn content (5%).	I. G. Farbenindustrie A.-G. (Lappe, Pier, Rumpf and Stern): G.P. 580,695, Kl 12o, July 14, 1933; add to G.P. 490,248, Kl 12o Gr 5, Feb. 25, 1923.
Reduction of CO.	Graphite (two types of oxidation).	Mayers: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 70-76 (1934).
Reduction of CO at ordinary pressure.	Fe—Cu (influence of alkali content).	Kodama and Fujimura: <i>Sci. Papers Inst. Phys. Chem. Research (Tokyo)</i> , <b>29</b> , 272-279 (1936).
Reduction of CO at ordinary pressure.	Fe—Cu (ratio of both metals investigated).	Fujimura: <i>Ibid.</i> , <b>29</b> , 280-284 (1936).
Reduction of CO by H <sub>2</sub> to hydrocarbons.	Catalyst mass divided into almost equal layers of 10-15mm. thickness.	Studien und Verwertungs Gesellschaft, m.b.H.: Norwegian P. 58,200, July 26, 1937.
Reduction of CO; T. 350-495°; atmospheric pressure; yield, 10-17% CH <sub>4</sub> . 2CO + H <sub>2</sub> → CH <sub>4</sub> + CO <sub>2</sub> under elevated pressure.	MoO <sub>3</sub> : ThO <sub>2</sub> = 1 : 1 + 10% BaO Cr <sub>2</sub> O <sub>3</sub> : MoO <sub>3</sub> = 1 : 1 + 10% BaO ThO <sub>2</sub> : MnO = 1 : 1 + K <sub>2</sub> CO <sub>3</sub> on kieselguhr Al <sub>2</sub> O <sub>3</sub> : MoO <sub>3</sub> = 7 : 3 + K <sub>2</sub> CO <sub>3</sub>	Bahr: <i>Ges. Abhandl. Kenntnis Kohle</i> , <b>12</b> , 292-297 (1937).
Reduction of CO by H <sub>2</sub> to hydrocarbons; T. 360-380°.	Catalyst indirectly heated by electricity; space filled with liquid products which form and the gas mixture enters the contact space from below; evaporation of liquid prevented by using a water condenser, entering gas finely distributed through a porous filter.	
Reduction of CO to a gas mixture containing more olefins (3.7%) than CH <sub>4</sub> (1.7%).	Ni—Cu catalyst activated at 275° and reduced at 248°.	Chakravarty: <i>Science and Culture</i> , <b>4</b> , 300-301 (1938).
Catalytic reduction of carbon monoxide to obtain a gas rich in CO <sub>2</sub> from residue gases of the benzene synthesis; yield, 97% CO <sub>2</sub> ; the gases remaining after separation of condensable ingredients and adsorption of hydrocarbons with low c.p. are treated in two stages with adsorption agents, e.g., active charcoal; by regeneration of second stage, e.g., with water vapor, the liberated gases are first separated.	Active charcoal.	Ruhrchemie, A.-G.: F.P. 836,701, Jan. 25, 1939.
Reduction of CO to 95% CH <sub>3</sub> OH, the remainder CH <sub>4</sub> and H <sub>2</sub> O (N—H mixture containing 0.5-1% CO is very suitable for NH <sub>3</sub> synthesis).	Hydrogenation catalysts (chiefly Cu or Zn) with 2 or more oxides, especially of the elements of the 3rd and 4th groups of the periodic system (Ce, Si, Al, Th, Zr).	Antoine Hème de Lacotte: F.P. 835,899, Jan. 5, 1939.

Table 3. Catalytic Reduction of Carbon Dioxide.

Reaction	Catalyst	Observer
Reduction of CO <sub>2</sub> .	Pt surface covered with BaO or W.	Srikantan: <i>Indian J. Phys.</i> , <b>5</b> , 685-698, (1930).
Reduction of CO <sub>2</sub> .	Ni, Ni—Cu, Ni magnetite (200°); Ni+(V, Mo, Zr, Si, Al, Cr oxides); Ni+(Th, Ce).	Selden Co. (Jaeger): U.S.P. 1,831,179, Nov. 10, 1931. Koch and Rusteo: <i>Brennstoff-Chem.</i> , <b>14</b> , 245 (1933). Bahr: <i>Ges. Abhandl. Kenntnis Kohle</i> , <b>8</b> , 219-227 (1928).
Reduction of CO <sub>2</sub> .	Strongly glowd carbon filament (1900°).	Sikooken: <i>Ann. Acad. Sci. Fennicae (A)</i> , <b>33</b> , (1931).
Reduction of CO <sub>2</sub> to CH <sub>4</sub> ; T. 156°.	Kieselguhr contacts used in benzene synthesis.	Fischer and Mayer: <i>Brennstoff-Chem.</i> , <b>12</b> , 225 (1931).

Table 3 (Continued).

Reaction	Catalyst	Observer
Reduction of CO <sub>2</sub> to CO; reduced to benzene hydrocarbons.	Kieselguhr-benzene contact.	Fischer and Koch: <i>Ibid.</i> , <b>13</b> , 428 (1932).
Reduction of CO <sub>2</sub> ; T. 150-200°.	Na <sub>2</sub> CO <sub>3</sub> on wood charcoal.	Edenholm and Widell: <i>Iva</i> , <b>1934</b> , 26-39 (April); (Refer to A. 1934 IV 26-39).
Reduction of CO <sub>2</sub> to hydrocarbon.	Catalyst poisoned by precipitation of non-volatile compounds in the course of synthesis and temp. increase; H <sub>2</sub> , H <sub>2</sub> O vapor, or a solvent may activate the catalyst.	Ruhrchemie A.-G.: Belg. P. 418,230, Nov. 4, 1936. Indian P. 22,776, April 15, 1936. (Refer to C. 1937 I 426).
Reduction of CO <sub>2</sub> : CO <sub>2</sub> + H <sub>2</sub> → CO + H <sub>2</sub> O; reaction velocity proportional to CO <sub>2</sub> pressure, but increases with H <sub>2</sub> pressure to a less extent than that corresponding to a direct proportionality; catalytic water gas reaction to be considered as a transfer of an O atom from CO <sub>2</sub> to H <sub>2</sub> under the action of O <sub>2</sub> adsorbed by Fe as an intermediate product.	Fe.	Doehlemann: <i>Z. Elektrochem.</i> , <b>44</b> , 178-183 (1938).

Table 4. Catalytic Reduction of Unsaturated Hydrocarbons.

Reaction	Catalyst	Observer
Reduction of C <sub>2</sub> H <sub>2</sub> to C <sub>2</sub> H <sub>4</sub> .	Cr sub-oxide in an acid medium.	Traube: G.P. 287,565, Kl 120, Gr 19, Aug. 6, 1913.
Reduction of C <sub>2</sub> H <sub>2</sub> to C <sub>2</sub> H <sub>4</sub> .		Kollitt: <i>Chem. Age (London)</i> , <b>5</b> , 88-90 (1920).
Reduction of C <sub>2</sub> H <sub>5</sub> O under H <sub>2</sub> pressure; products between Et(OH) and EtOCH <sub>2</sub> CH <sub>2</sub> OH are obtained.	Ni-BaO.	Rheinische Kampfer Fabrik (Kattol): G.P. 563,625, March 20, 1931.
Reduction of olefins in alcoholic solution (olefins readily form peroxides).	PtO <sub>2</sub> (Fe slows down the reaction).	Thomson: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 2744-2747 (1934). Kern, Shriner and Adams: (Refer to C. 1925 II 170).
Reduction of ethylene chlorhydrin under H <sub>2</sub> pressure.	Acceleration by NaOH is greater than by Ca(OH) <sub>2</sub> , which is greater than by CaCO <sub>3</sub> ; Ni on silica gel prepared from Ni(NO <sub>3</sub> ) <sub>2</sub> ; Ni(NO <sub>3</sub> ) <sub>2</sub> precipitated on Si gel suspension + NaOH; Ni(NO <sub>3</sub> ) <sub>2</sub> + HNO <sub>3</sub> precipitated on water glass.	Uschakow and Michailow: <i>Zhur. Obshchei Khim.</i> , <b>7</b> (69), 249-252 (1937).

Table 5. Catalytic Reduction of Organic Halides.

Reaction	Catalyst	Observer
Reduction of organic halides.		Borsh and Heimbürger: <i>Ber.</i> , <b>48</b> , 452 (1915).
Reduction of organic halides.	Pd on CaCO <sub>3</sub> .	Bush and Stove: <i>Ber.</i> , <b>49</b> , 1063-1071 (1916).
Reduction of organic halides.		Rosenmund and Zetsche: <i>Ber.</i> , <b>50</b> (1917); <b>51</b> , 578-585 (1918).
Reduction of organic halides.	Hydrazine.	Busch: <i>Z. angew. Chem.</i> , <b>31</b> , 232 (1918).
Reduction of acid chlorides.	P oxychloride.	Zetsche and Arndt: <i>Helv. Chim. Acta</i> , <b>8</b> , 591 (1925).
Reduction of acid chlorides under decreased pressure.		Grignard and Mingasson: <i>Compt. rend.</i> , <b>185</b> , 1173-1176 (1927).

Table 6. Catalytic Reduction of Organic Acids.

Reaction	Catalyst	Observer
Reduction of acids and alkalies and polybasic and hydroxy-acids.	Combined action of catalysts.	Mitscherling: U.S.P. 1,432,775, Oct. 24, 1922. Ipatieff and Razuvaev: <i>Ber.</i> , <b>60</b> , 1973 (1929). Ipatieff and Razuvaev: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>59</b> , 1083 (1927).
Reduction of monobasic oxy-acids: lactic acid to methyl succinic acid; pyroracemic acid to methyl succinic acid.	NiO + Al <sub>2</sub> O <sub>3</sub> .	Ipatieff and Razuvaev: <i>Ber.</i> , <b>59</b> , 2028 (1926); <b>60</b> , 1976 (1927).
Reduction of dibasic oxy-acids: Na salt of maleic acid or tartaric acid to succinic acid.		
Reduction of: cinnamic acid to hydrocinnamic acid; oleic acid to stearic acid; eugenol to hydroeugenol; cumarin to hydrocumin, using Tetralin as a H <sub>2</sub> donator T. 115-120°.	Pd black.	Akabori and Suzuki: <i>Proc. Imp. Acad. (Tokyo)</i> , <b>5</b> , 255-256 (1930).
Partial reduction of phenyl propionic acid to cinnamic acid.	Metals in aqueous NH <sub>3</sub> solution with the addition of NH <sub>4</sub> Cl at 20°.	Ott: <i>Ber.</i> , <b>67</b> , 1669-1674 (1934).
Reduction of carbocyclic acids to carbocyclic alcohols; T. 300-400°; pressure, 100-250 atm.	Oxides of Cu, Cd, Ni, Co, Zn, Sn, Mg, and Mn.	Imperial Chemical Industries, Ltd.: E.P. 417,582 (1934).
Reduction of aliphatic carboxylic acids in the presence of lower aliphatic alcohols to high molecular weight aliphatic alcohols with at least 8 carbon atoms.	Cu acetate solution on kieselguhr; 15% metallic Cu and 85% kieselguhr.	Th. Böhme A.-G. (Normann and Pruckner): G.P. 594,481 (1934).
Reduction of aliphatic acids to aliphatic alcohols and to aliphatic esters: butyric acid to ethyl butyrate; T. 310-340°; isovaleric acid to iso-valerate; T. 350-360°; acetic acid to ethyl acetate T. 340°.	Oxides of Cr or Th + Cu, Ag or Ni; likewise on silicic acid gel.	Kessler Chemical Corporation (Goldmann and Littmann): U.S.P. 1,997,172 (1935).
Reduction of mixed anhydrides or organic carboxy-acids and inorganic oxy-acids, e.g., silicic acid, stearic acid anhydride.	37 p. Ni carbonate on kieselguhr activated by Cr or V compounds.	Henkel & Co. (Hintermaier): G.P. 622,649 (1936).
Reduction of acrylic acid nitrile to the corresponding amino-ether; 265 p. acrylic acid nitrile + 740 p. butanol at 40° is condensed to <i>n</i> -butyloxy- <i>n</i> -propionitrile and forms, in addition to secondary amines, <i>n</i> -butyloxy- <i>n</i> -propyl amine; T. 70-110°; H <sub>2</sub> pressure, 25 atm.	2Na.  Ni.	I. G. Farbenindustrie A.-G.: F.P. 796,001, March 27, 1936.
Reduction of fatty acids with more than 8 carbon atoms to aliphatic alcohols (high temp. and pressure).	Commercial CuCO <sub>3</sub> .	Böhme Fettchemie Gesellschaft m.b.H. (Normann): G.P. 648,510, Kl 12o, Aug. 3, 1937.

Table 7. Catalytic Reduction of Carbonic Acid.

Reaction	Catalyst	Observer
Reduction of H <sub>2</sub> CO <sub>3</sub> to CH <sub>4</sub> .		Sabatier and Senderens: <i>Compt. rend.</i> , <b>134</b> , 689 (1902).
Reduction of H <sub>2</sub> CO <sub>3</sub> .	Inducted intramolecular rearrangement of siloxene acid derivatives.	Kautsky: <i>Ber.</i> , <b>64</b> , 1610-1622 (1931).
Reduction of H <sub>2</sub> CO <sub>3</sub> (dissolved in low molecular alcohols) by H <sub>2</sub> at 200-400° under 13.5-200 atm. pressure; alcohols formed at conversion pressure and esters of initial acids with alcohols obtained by rapid passage of acids through the reaction vessel.	Metal oxides or chromites of Zn, Cu or Cd.	Dupont (Lazier): U.S.P. 1,839,974, Jan. 5, 1932.

Table 7 (Continued).

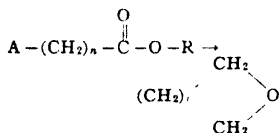
Reaction	Catalyst	Observer
Reduction of non-aromatic carboxy-acids; T. greater than 300°; pressure above 25 atm.	H <sub>2</sub> .	Canadian Industries, Ltd. (Lazier): Can. P. 347,168, Jan. 1, 1935.
Reduction of H <sub>2</sub> CO <sub>3</sub> to CH <sub>4</sub> ; T. above 300°; (below 300°, only CO formation takes place).	Pure Fe; Cu, Co and Ni serve as activators.	Küster: <i>Brennstoff-Chem.</i> , 17 203-206 (1936).
Reduction of H <sub>2</sub> CO <sub>3</sub> at atmospheric pressure; temp. above 300°; yield, 16.7% liquid hydrocarbons and 46.4% gaseous hydrocarbons; reaction mechanism: (1) reduction of CO <sub>2</sub> to CO; (2) conversion into hydrocarbons as in the benzene synthesis by Fisher and Tropach.	Fe + Cu (only by strong alkalization) (5Co + 5Fe + 0.5 Cu + 1% K <sub>2</sub> CO <sub>3</sub> ) on kieselguhr.	Küster: <i>Brennstoff-Chem.</i> , 17 221-228 (1936).
Reduction of acid amides to amines; carbonic acid amides with H <sub>2</sub> under pressure reduced to amines; lauric acid amide to mono- and didodecylamine (4 hrs.); T. 270°; 200 atm.; stearic acid methyl amide to methyl octodecylamine.	Al-Co nitrate precipitated with Na <sub>2</sub> CO <sub>3</sub> .	I. G. Farbenindustrie A.-G.: E.P. 421,196 (1934).

Table 8. Catalytic Reduction of Ketones.

Reaction	Catalyst	Observer
Reduction of ketones.	CuO and Zn dust.	Vavon: <i>Compt. rend.</i> , 155, 286 (1910). Ipatieff and Balatchinsky: <i>J. Russ. Phys.-Chem. Soc.</i> , 43, 1828 (1911). Ipatieff and Balatchinsky: <i>Ber.</i> , 44, 3459 (1911).
Reduction of acetone by Mg.	Water-free AlCl <sub>3</sub> .	Uschakow: <i>Z. anorg. allgem. Chem.</i> , 183, 140-150 (1929).
Reduction of acetone to isopropyl alcohol; propylene not formed (industrial process).	Oxides of Mg, Zn, Al, Si, Ti, Se in a mixture with K <sub>2</sub> CO <sub>3</sub> (the alkali, or alkaline-earth metals are added to prevent possible splitting off of water; Zn chromate + 10% potash).	Dupont: F.P. 671,705 (1929).
Reduction of acetone to isopropyl alcohol.	Cu—Cr or Zn—Cr alloy oxidized by HNO <sub>3</sub> .	Maxted: E.P. 378,943, Sept. 15, 1932.
Reduction of oxyketones obtained by condensation of aldehydes or ketones to the corresponding alcohols; T. 100°; 25 atm. pressure.	Chromium on kieselguhr.	I. G. Farbenindustrie A.-G. (Müller and Hoffmann): G.P. 558,645 (1932).
Reduction of aromatic ketones at room temp. and atmospheric pressure.	10% Pt plated charcoal + alcoholic Pd chloride solution.	Zelinsky, Packendorff and Leder-Packendorff: <i>Ber.</i> , 66, 872 (1933).
Reduction of acetophenone to ethyl benzene, and <i>p</i> -methyl-acetophenone to <i>p</i> -ethyl toluene.		
Reduction of propionphenone in alcoholic solution direct to propyl benzene (phenyl ethyl carbinol is not formed as an intermediary product).	Pd on bone charcoal.	Hartung and Crossley: <i>J. Am. Chem. Soc.</i> , 56, 158-159 (1934).
Reduction of diphenyltriketone: (1) C <sub>6</sub> H <sub>5</sub> CO · CO · CO · C <sub>6</sub> H <sub>5</sub> → (2) C <sub>6</sub> H <sub>5</sub> COCH(OH)COC <sub>6</sub> H <sub>5</sub> ↓ C <sub>6</sub> H <sub>5</sub> CH(OH)CH(OH)CH(OH)C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> CH(OH)COCH(OH)C <sub>6</sub> H <sub>5</sub> ⇌ (3) C <sub>6</sub> H <sub>5</sub> CH(OH)CH(OH)COC <sub>6</sub> H <sub>5</sub>	Pt—PtO <sub>2</sub> .	Bigelow, Rule and Black: <i>J. Chem. Soc.</i> , , 83-85 (1935).
Reduction of carbonyl compounds in the production of motor fuel hydrocarbons from purified water gas.	A catalyst containing a permuto-genetic material.	Selden Co. (Jaeger): U.S.P. 1,925,387.

Table 8 (Continued).

Reaction	Catalyst	Observer
Reduction of carbonyl compounds, oxides of carbon, ketones, aldehydes, acids, esters; reduction, stepwise; $\text{CH}_3\text{OH}$ obtained from $\text{CO}$ and $\text{H}_2$ at 300–370° and 85–150 atm. pressure.	Base exchangers, e.g., metal compounds reduced with soluble silicates to form zeolites of the type of Al silicate or double silicate.	Selden Co.; F.P. 669,872, Nov. 21, 1929.
Reduction of ketones: mesityl oxide to methylisobutyl carbinol; T. 120–125° at ordinary pressure; yield, 85–90%.	Cu or Ni on kieselguhr or silica gel.	Société Anonyme des Destilleries des Deux-Severs (Guinot); G.P. 641,217 (1937). Ipatieff: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>44</b> , 1703 (1912). Skita: <i>Ber.</i> , <b>45</b> , 3218 (1913); <b>48</b> , 1486 (1916).
Preparation of cyclic ether by reduction of $\gamma$ or $\delta$ oxy-keto carboxyl compounds or 1,2- or 1,3-dicarboxyl compounds with $\text{H}_2$ ; T. 200–500°; better 240–400°; pressures 30–650 atm.; reaction course.	Hydrogenation catalysts; 1500 g. copper nitrate in 4 liters $\text{H}_2\text{O}$ are mixed with 1000 g. ammonium chromate in 1 l. $\text{H}_2\text{O}$ and the originated free acid is neutralized with $\text{NH}_4\text{OH}$ ; copper ammonium nitrate precipitate after washing and drying is heated to 400°, twice extracted with 10% acetic acid, washed and dried; 10 g. copper chromite powder obtained.	E. I. du Pont de Nemours & Co. (Lazier); U.S.P. 2,130,501, Sept. 20, 1938.



where  $n=2$  or 3;  $\text{R}=\text{H}$ , or a hydrocarbon group, and  $\text{A}=\text{acyl}$ , a carboxylic, or oxy-methylene group; 100 g. levulinic acid and ethyl butyrate heated to 250° with 10 g. butanol in steel pressure vessel;  $\text{H}_2$  pressure 3000 lbs./sq. in.; yield 40%; from 150 g. ethyl citrate and 25 g. trimethyl propane, methyl tetrahydrofuran and an ether of unknown composition is obtained.

Table 9. Catalytic Reduction of Oximes.

Reaction	Catalyst	Observer
Reduction of oximes.	Colloidal Pd.	Gulewitsch: <i>Ber.</i> , <b>57</b> , 1645–1653 (1924).
Reduction of aliphatic oximes at room temp.	Ni.	Wassiljew: <i>Ber.</i> , <b>60</b> , 1122–1125 (1927).
Reduction of oximes to primary amines; benzaldoxime to benzylamine in absolute alcohol; the presence of $\text{HCl}$ prevents the formation of secondary amines.	Pd on charcoal.	Hartung: <i>J. Am. Chem. Soc.</i> , <b>50</b> , 3370 (1928). I. G. Farbenindustrie A.-G.; F.P. 621, 434, 1927; (Refer to C. 1927 II 977).

Table 10. Catalytic Reduction of Higher Alcohols.

Reaction	Catalyst	Observer
Reduction of borneol to isocamphane in a stream of $\text{H}_2$ ; T. 220°.	$\text{NiO} + \text{Al}_2\text{O}_3$ .	Ipatieff: <i>Ber.</i> , <b>45</b> , 3205 (1912).
Reduction of allyl alcohol to propyl alcohol.	Ni formate.	Fettindustrie Gesellschaft m.b.H. (Bremen); G.P. 329,471, Kl 12o, Gr 27, Jan. 23, 1912; add to G.P. 312,668.
Reduction of alkyl furyl carbinol.	Pt oxide.	Pierce and Adams: <i>J. Am. Chem. Soc.</i> , <b>47</b> , 1047–1063, 1098–1104 (1925).
Reduction of hydro-aromatic alcohols.		Rheinische Kampfer Fabrik (Schöllkopf); G.P. 432, 802, Kl 12g.

Table 10 (Continued).

Reaction	Catalyst	Observer
Reduction of aromatic alcohols: triphenyl carbinol to triphenyl methane; diphenyl carbinol to diphenylmethyl methane; dimethylbenzyl carbinol to dimethylbenzyl methane; in a stream of $H_2$ , T. 180° in the absence of $H_2$ , T. 300°.	Active charcoal.	Zelinsky and Gawerdowska: <i>Ber.</i> 61, 1049 (1928).
Reduction of tertiary aliphatic and aliphatic aromatic alcohols to the corresponding hydrocarbons; T. 300°.	Pt plated charcoal; active charcoal.	Zelinsky and Gawerdowska: <i>Ber.</i> 64, 435 (1931).
Reduction of high molecular polyvalent alcohols to low molecular polyvalent alcohols.	Ni or Co + $Al_2O_3$ .	Dupont (Rothrock): U.S.P. 2,004,135 (1935).
Reduction of higher alcohols.	Zn dust in ether.	
Reduction of higher alcohols.	$Cr_2O_3$ ; Cr-containing catalyst.	
Reduction of higher alcohols.	Fe (prepared from $FeCl_3$ ).	
Reduction of higher alcohols.	Mg in ether.	
Reduction of higher alcohols.	Ni (prepared from dehydrated $NiBr_2$ ).	
Reduction of higher alcohols.	Mg or Zn.	
Reduction of higher alcohols at temp. not higher than 200° so that $MgCO_3$ will not be decomposed.	$Cu + MgCO_3$ .	
Reduction of higher alcohols.	Cu (reduced from Cu oxalate and CuO).	
Reduction of higher alcohols.	Cu (obtained from Cu oxalate; 5 times more active than by reduction from CuO).	
Reduction of higher alcohols; acetaldo $\beta$ -oxybutyric aldehyde to 1,3-butylene glycol).	Ni + NiO (less than 50% Cu-Co-Fe added on kieselguhr).	Dalmer: G.P. 394,116 (1924).
Reduction of higher alcohols; acetaldo in an acid medium to butylene glycol; T. below 80°.	Reduced Cu on silica gel.	I. G. Farbenindustrie A.-G. (Müller): G.P. 548,814 (1931). E.P. 348,248 (1930).
Reduction of higher alcohols; paraldo to 1,3-butylene glycol; T. 30–50°; pressure, 20–25 atm.	Cu, Ni, Co, Pt, Pd on kieselguhr.	I. G. Farbenindustrie A.-G. (Leopold and Heyse): G. P. 526,477 (1931); P.P. 689,092 (1930).

Table 11. Catalytic Reduction of Esters.

Reaction	Catalyst	Observer
Reduction of carboxylic acid esters containing at least 2 carbon atoms.	Active hydrogenation catalysts.	I. G. Farbenindustrie A.-G.: Belg. P. 367,646, Aug. 25, 1930.
Reduction of carboxylic acid esters under high temperature and pressure; T. 200°, pressure 100 atm. $H_2$ ; $BzOEt$ , $PhCH_2CO_2Et$ . $O-HOC_6H_4CO_2Et$ ; addition of $H_2$ in $C_6H_5$ nucleus forms hexahydro- compounds.	Ni.	Mitsui: <i>J. Chem. Soc. Japan</i> , 54, 29:–36 (1933).
Reduction of hexahydro- <i>o</i> -toluene carboxylic acid esters to 2-methyl cyclohexyl carbinol T. 325°; pressure 250 atm.	$ZnO-Cu$ on kieselguhr.	Imperial Chemical Industries, Ltd.: E.P. 417,582 (1934).
Reduction of high molecular fatty acid esters heated with palmolive oil; T. 350° pressure 100 atm. $H_2$ .	Ni on kieselguhr.	Deutsche Hydrierwerke A.-G. (Schrauth): G.P. 629,244 (1936).

Table 11 (Continued).

Reaction	Catalyst	Observer
Reduction of naphthenic acid esters to naphthene; T. 300–350°; pressure, 50 atm.	Ni on kieselguhr.	Deutsche Hydrierwerke A.-G. (Schrauth); G.P. 636,681 (1936).
Reduction of carboxylic acid esters; ethyl laurate; T. 350°; pressure, 100–200 atm.	Cu compound on kieselguhr (2% by weight of the ester).	Böhme Fettchemie Gesellschaft m.b.H. G.P. 639,527 (1937).
Reduction of esters in liquid phase to alcohols; T. 100–300°; pressure up to 500 atm.	Cu-Ba-Cr; Cu-Ca-Cr.	Röhm and Haas Co. (Adkins, Folkers and Connor); U.S.P. 2,091,800, Aug. 31, 1937.
Reduction of esters to corresponding alcohols.	CuO and active Al <sub>2</sub> O <sub>3</sub> ; instead of Al <sub>2</sub> O <sub>3</sub> alone or their mixture, other difficultly reducible metal oxides, such as Cr, Si, Ba may be used; likewise as carriers may be applied pumice, infusorial earth, silica gel (this catalyst may be used successfully for the preparation of amines from amides or nitro-compounds).	Röhm and Haas Co. (Andrews); U.S.P. 2,118,001, May 17, 1938.
Reduction of organic acids, esters or anhydrides with more than one carbon atom in the molecule, e.g., ethyl acetate to acetaldehyde; lauric acid to the corresponding aldehyde; T. greater than 300° (300–400°); pressure, 10 atm. H <sub>2</sub> .	Zn, Cd, or Cu chromite; elemental Ni, Fe and Co cause hydrocarbon formation.	Dupont (Lazier); U.S.P. 2,105,540, Jan. 18, 1938.

Table 12. Catalytic Reduction of Phenols.

Reaction	Catalyst	Observer
Reduction of phenols with H <sub>2</sub> at high temp. and medium pressure to hydro-aromatic alcohols (nucleus hydrogenation and retaining of the OH group).	Ni on kieselguhr.	Brochet: E.P. 16,936 (1913). E.P. 22,523 (1913).
Reduction of phenol directly to cyclohexanol.	Cu–Mg and Ni–Mg alloys.	Badische Anilin- und Soda Fabrik: G.P. 408,811, Kl 12o, Gr 27, Jan. 24, 1925.
Reduction of phenols under H <sub>2</sub> pressure.	Al <sub>2</sub> O <sub>3</sub> .	Kling and Florentine: <i>Bull. soc. chim.</i> (4), 41, 1341 (1927).
Reduction of phenol; T. 480°; pressure, 70–80 kg./cm.; yield, 13% aliphatic hydrocarbons and 72% benzene; 75% phenol converted into benzene at 750°.	5% Al <sub>2</sub> O <sub>3</sub> ; Al <sub>2</sub> O <sub>3</sub> +MoO <sub>3</sub> .	Kling and Florentine: <i>Compt. rend.</i> , 184, 885 (1927); 193, 859, 1023 (1931). Kling and Florentine: E.P. 263,082. Société de Carburants Synthétiques: F.P. 733,384 (1932).
Reduction of phenol to aromatic hydrocarbons; T. 700°; pressure, 50 atm.; toluene to toluol; T. 600–630°; 10–12 atm. pressure; 97–98% yield.	Well-glowed charcoal.	Karpati and Hübsch: Hung. P. 96,334.
Reduction of mixtures of ketones and <i>p</i> -nitrophenol to nitroso-phenol by H <sub>2</sub> ; from <i>p</i> -nitrophenol as well as nitroso-phenol in an acetone solution <i>p</i> -oxyphenylhydroxylamine, <i>p</i> -isopropyl aminophenol are formed.	Pt oxide.	Miller and Kilpatrick: <i>J. Am. Chem. Soc.</i> , 53, 3217 (1931).
Reduction of organic compounds: phenols, pyridine derivatives, aromatic and aliphatic aldehydes and heterocyclic compounds.	Pt oxide obtained by melting PtCl <sub>2</sub> H <sub>2</sub> with NaNO <sub>2</sub> (excellent catalyst); velocity of reduction greater than with Pt black.	Vorhees and Adams: <i>J. Am. Chem. Soc.</i> , 54B, 97–1405 (1932).
Reduction of gaseous phenols; high H <sub>2</sub> pressure; T. 400–500° the partial pressure is held low and from time to time only a part of the phenols are introduced, e.g., 60–90% is reduced; thus the formation of hydrogenated hydrocarbons is avoided.	Catalyst favoring the reduction of the OH group, e.g., those containing sulfides or selenides of Mo, W, V.	I. G. Farbenindustrie A.-G.: F.P. 743,570, April 3, 1933.

Table 12 (Continued)

Reaction	Catalyst	Observer
Reduction of phenol to aromatic hydrocarbons; T. 250–550°.	NH <sub>4</sub> vanadate.	Gas. Light and Coke Co. (Griffith and Dalrymple); E.P. 403,708 (1933).
Reduction of tar phenols to benzene hydrocarbons; phenols may be reduced to aromatic hydrocarbons (without splitting off the methyl group); besides aromatic hydrocarbons, small amounts of ether are formed; reduction of phenols, cresols, xylenols, di-oxybenzenes, naphthols, as well as commercial phenol and cresol-containing oils and tar fractions; excess pressure up to 20 atm. promotes hydrogenation.	Mo, W, Cr, U, Zn, Al or their mixtures; highly active Mo contacts obtained by dissolving Mo in HNO <sub>3</sub> and igniting the nitrate at 350–440° (ordinary pressure).	Fischer, Bahr and Petrick: <i>Brennstoff-Chem.</i> , <b>13</b> , 45–46 (1932).
Reduction of tar phenols to benzene hydrocarbons; T. 360–380°; by-products, high-boiling hydrocarbons, but are not formed by ring fracture; demethylation hydrogenation.	MoO <sub>3</sub> .	Bahr and Petrick: <i>Brennstoff-Chem.</i> , <b>14</b> , 161–165 (1933).
Reduction of tar phenols (m-cresol and cresol mixtures); CO instead of H <sub>2</sub> was used; essential yield of toluene is obtained over Cu, Cu–Ba chromates and W oxides.	MoO <sub>3</sub> ; Fe–Cu and V <sub>2</sub> O <sub>5</sub> .	Bahr and Wedeking: <i>Ges. Abhandl. Kennis Kohle</i> , <b>12</b> , 183–197 (1937).

Table 13. Catalytic Reduction of Cresols.

Reaction	Catalyst	Observer
Reduction of cresol to toluene; T. 480–500°.	Asbestos impregnated with Fe nitrate (precipitated iron hydroxide with NH <sub>3</sub> ).	Stadnikoff, Gawriloff and Winogradoff: <i>Brennstoff-Chem.</i> , <b>7</b> (1926).
Reduction of crude cresol to aromatic and hydro-aromatic hydrocarbons; T. 460°; 200 atm. pressure.	NH <sub>4</sub> vanadate and Al <sub>2</sub> O <sub>3</sub> .	I. G. Farbenindustrie A.-G.: F.P. 295,947 (1928).
Reduction of cresol to toluene and benzene; T. 450°.	Al <sub>2</sub> O <sub>3</sub> + Fe.	I. G. Farbenindustrie A.-G.: E.P. 283,600 (1928). F.P. 612,908 (1926).

Table 14. Catalytic Reduction of Aromatic Aldehydes.

Reaction	Catalyst	Observer
Reduction of benzaldehyde to benzyl alcohol; nitrobenzene to aniline, and benzylidene acetone to phenylbutanone.	Pt and Pd chlorides.	Nibière: <i>Bull. soc., chim.</i> , <b>29</b> , 217–219 (1920).
Reduction of cinnamic aldehyde to alcohol.	Pt oxide and Pt black.	Skita and Keil: <i>Ber.</i> , <b>61</b> , 1452–1459 (1928).
Reduction of aromatic aldehydes to corresponding phenols.	Metal salts the hydroxides of which are soluble in excess NH <sub>3</sub> ; precipitated on kieselguhr, silica gel, alumina gel, active charcoal, or fuller's earth.	Dupont:

Table 15. Catalytic Reduction of Aliphatic Aldehydes.

Reaction	Catalyst	Observer
Reduction of aldehyde sulfite compounds to aldehyde sulfoxylates.	Ni on kieselguhr.	I. G. Farbenindustrie A.-G.: F.P. 641,509 (1929).
Reduction of aliphatic aldehydes to primary alcohols; 15 parts Ca octylate and 15 parts Ca formate in 60 parts lauric alcohol; T. 350°; pressure, 110 atm.; pressure increases by heating to 220 atm.; yield of octyl alcohol, 95%.	Hydrogenation catalyst on kieselguhr (CuCO <sub>3</sub> ).	Th. Böhme A.-G. (Prückner): G.P. 574,834 (1933).



Table 16. Catalytic Reduction of Aromatic Nitro- Compounds.

Reaction	Catalyst	Observer
Reduction of aromatic amines under ordinary pressure.	Reduced Ni.	Sabatier and Senderens: <i>Ann. chim. phys.</i> (8), 382 (1905).
Reduction of nitrocymol to aminocymol.	Fe, HCl +catalyst.	Austrian P. 96,518, April 10, 1919.
Reduction of aromatic nitro-compounds to the corresponding amines.	Bone charcoal, wood charcoal, ZnCl <sub>2</sub> .	Farbenfabriken vorm Friederich Bayer & Co. (Engelhardt): G.P. 388,185, Kl 12a Gr 3, May 20, 1921.
Reduction of aromatic nitro-compounds to the corresponding amines.		I. G. Farbenindustrie A.-G.: E.P. 260,186, Nov. 18, 1926.
Reduction of aromatic nitro-compounds to the corresponding amines.	Cu, Ag, Au, Fe, Zn, Pb, Sn and their oxides or carbonates.	I. G. Farbenindustrie A.-G. (Schmidt and Feller): G.P. 436,820, Cl 12g, Nov. 9, 1926.
Reduction of secondary and tertiary amines of the general formula: aryl NRR' to primary and secondary amines: R-H <sub>2</sub> , or a benzyl group, R'; 50 $\mu$ . <i>n</i> -ethylbenzyl aniline +200 cc. alcohol; to one molecule of H <sub>2</sub> is taken up.	Metal catalyst on active charcoal; Pd. charcoal.	Merck & Co., Inc. (Krauss): G.P. 432,151 (1926).
Reduction of aromatic nitro-compounds to the corresponding amines with H <sub>2</sub> .	Pt oxide-Pt black.	Adams, Cohen and Rees: <i>J. Am. Chem. Soc.</i> , 49, 1093-1099 (1927).
Reduction of aromatic nitro-compounds to the corresponding amines.		I. G. Farbenindustrie A.-G.: E.P. 260,185, Nov. 18, 1926. F.P. 617,559, Feb. 22, 1927.
Reduction of aromatic nitro-compounds to primary amines of the benzene series at 100° and pressure not less than 20 atm.; from nitrobenzene, aniline is obtained, and no hydrogenation of the benzene ring takes place.	Heavy metals of the 2nd to 8th groups: Cu, Ag, Au, as well as silica: 1-2% S or its compounds is added; nitro-compounds containing considerable amount of thiophene derivatives may also be used.	I. G. Farbenindustrie A.-G.: E.P. 295,824, Sept. 13, 1928. E.P. 297,212, Oct. 11, 1928. F.P. 639,557, 1928. (Refer to C. 1929 I 3143).
Reduction of aromatic nitro-compounds in liquid phase to amines.	0.52 g. Ni for each gram of the compound reduced.	Brown, Etzel and Henke: <i>J. Phys. Chem.</i> , 32, 631-635 (1928).
Reduction and hydrogenation of aromatic nitro-compounds.		Selden Co. (Jaeger): E.P. 304,640, March 20, 1929. U.S.P. 1,850,797, March 22, 1932.
Reduction of aromatic nitro-compounds with H <sub>2</sub> .	Pt black.	Verseley and Rein: <i>Collection Czechoslov. Chem. Commun.</i> , 1, 360-367 (1929).
Reduction of aromatic nitro-compounds.	Cu chromate, V oxide.	Doyal and Brown: <i>J. Phys. Chem.</i> , 36, 1549-1561 (1932).
Reduction of difficultly reducible aromatic nitro-compounds: homopiperonylamine to primary amines.	A suspension of 2 g. Pd black in a mixture of 100 cc. CH <sub>3</sub> COOH with 2 cc. conc. H <sub>2</sub> SO <sub>4</sub> heated under stirring with H <sub>2</sub> at 6° at 3 atm. pressure.	Peschke: G.P. 511,794, Kl 12o, March 15, 1933.
Reduction of aromatic nitro-compounds to amines with H <sub>2</sub> .	Ni nitrate whose activity is changed by the addition of sulfides or chlorides; mixed with metals: Ag, Cu, Fe. or difficultly reducible oxides: Al, Zn; silicic acid, anhydride, kieselguhr, or pumice as carriers.	Kenkyujo, Furakawa and Kubote: <i>Jap. P.</i> 101,254, July 5, 1933.
Reduction of aromatic nitro-compounds: nitroxylenes, to xylidines with H <sub>2</sub> .	Ni with methyl oleate and methyl palmitate; ethyl oxalate acts somewhat anti-catalytically; accelerated action related to presence of long C chains and based upon the degree of dispersion of the Ni.	Green: <i>J. Soc. Chem. Ind.</i> , 52, 172-173 (1933).

Table 16 (Continued).

Reaction	Catalyst	Observer
Reduction of aromatic nitro-compounds (for example ditolyl-unsym.-diphenyl-xylyl naphthyl-ethyl-butyl triphenyl-nitroguanidine, etc.); to prevent decomposition of aminoguanidine, buffer-acting compounds, such as $MgSO_4$ , or a mixture of alkali phosphates, $Na_2B_4O_7$ with $B(OH)_3$ and $NaCl$ may be added.	Metal catalysts: Ni, Fe, Co, Pt, Pd, and Rh.	Dupont (M. Gill): U.S.P. 2,033,203, March 10, 1936.
Reduction of aromatic nitro-compounds to $\beta$ -arylhydroxylamines at room temp.; yield: 58.4% phenylhydroxylamine 59.8% o-tolylhydroxylamine 56.1% m-tolylhydroxylamine 69.5% o-anisylhydroxylamine 69.5% o-phenetylhydroxylamine.  In case of reduction in dilute mineral acid instead of acetic acid solution, as intermediate products, besides nitroso-compounds, are formed arylhydroxylamine compounds which at once are reduced further to amines.	Zn dust in $CH_3COOH$ solution; Pb and Cd may be used.	Lukaschewitsch: <i>Zhur. Obshchei Khim.</i> 7 (69), 2209-2225 (1937).
Reduction of aromatic nitro-compounds: nitrobenzene in conc. HCl; yield, large amount of chloranilin: 10% chloranilin 8% chloranilin 0% chloranilin traces chloranilin phenylhydroxylamine readily converted to anilin.	69% Sn. 58% Hg.  Zn. SnCl <sub>2</sub> . CuCl <sub>2</sub> . FeCl <sub>2</sub> .	Lukaschewitsch: <i>Ibid.</i> , 7 (69), 2209-2225 (1937).
Reduction of o-nitrocinnamic acid nitriles, e.g., o-nitro- $\alpha$ -phenyl cinnamic acid nitrile to N-oxy- $\alpha$ -amino- $\beta$ -phenyl quinoline (originating eventually by a rearrangement of the first formed hydroxylamine).	Pd-kieselguhr.	Bauer: <i>Ber.</i> , 71, 2226-2229 (1938).
Reduction of corresponding nitriles to the amines and conversion of the latter with Na nitrite to prepare monovalent alcohols with 6 and more C atoms in the molecule, such as hexyl-, decyl-, dodecyl-, octadecyl alcohols; (reduction is carried out in an acid solution).	Pt.	Armour & Co.: E.P. 494,666, Nov. 24, 1938.
Reduction-alkylation of primary aromatic amines according to the assumed mechanism:		Emerson and Walters: <i>J. Am. Chem. Soc.</i> , 60, 2023-2025 (1938).

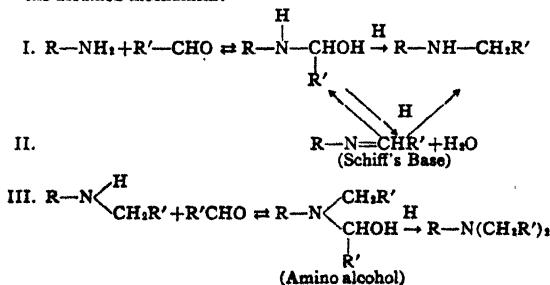


Table 16 (Continued).

Reaction	Catalyst	Observer
<i>e.g.</i> , from aniline and aldehydes, <i>n</i> -alkylaniline obtained in a yield of 47-65%.	Best action obtained with Raney Ni as a reduction catalyst and Na acetate as a condensation agent; it is assumed that, for carrying out reduction with primary aromatic amines as reducing agents, one that is sufficiently strong to reduce the amino-alcohol should be used, and the condensation agent should act so mildly that dehydration and polymerization are avoided.	Wallach: <i>Ann.</i> , <b>343</b> , 54 (1906). Clarke, Gillespie and Weiss- haus: <i>J. Am. Chem. Soc.</i> , <b>55</b> , 457-87 (1933); (Refer to C. 1934 I 1472).

Table 17. Catalytic Reduction of Nitrobenzene.

Reaction	Catalyst	Observer
Reduction of nitrobenzene to aniline.		Badische Anilin- und Soda Fabrik:
Reduction of nitrobenzene and nitrotoluene to aromatic amines in the presence of H <sub>2</sub> O; T. 330-350°; pressure, 30 atm.	Al <sub>2</sub> O <sub>3</sub> ; kieselguhr + Al <sub>2</sub> O <sub>3</sub> .	von Girssewald: G.P. 281,100 (1915). G.P. 343,324 (1921).
Reduction of nitrobenzene to aniline at 270°.	Butyl alcohol with CuO.	Legg and Adam: E.P. 166,283, Aug. 11, 1921.
Reduction of nitrobenzene to amine at 200°.	Silica gel charged with Cu(OH) <sub>2</sub> .	Badische Anilin- und Soda Fabrik: G.P. 352,439 (1922). I. G. Farbenindustrie A.-G.: E.P. 260,186 (1927). F.P. 617,559 (1927).
Reduction of nitrobenzene to aniline in the gaseous phase.		Semeria, Milone and Letti: Atti accad. sci. Torino, 637 (1927).
Reduction of $\alpha$ -nitronaphthalene in an alcoholic solution to $\alpha$ -naphthylamine; T. 70-80°; $\alpha$ -nitrobenzene sulfonic acid; T. 70-90°.	Ni nitrate (70°) and silica gel + a very dilute Na <sub>2</sub> CO <sub>3</sub> solution added dropwise during 8 hrs.	I. G. Farbenindustrie A.-G.: F.P. 621,434 (1927).
Reduction of nitrobenzene to aniline to azobenzene to hydrazobenzene, ammonia and cyclic compounds.	Titanium.	Etzel: <i>J. Phys. Chem.</i> , <b>32</b> , 852-860 (1928).
Reduction of commercial nitrobenzene to aniline; 6 hrs.; T. 180°; 140 atm. H <sub>2</sub> pressure; T. 100°; pressure not less than 20 atm.; 1-2% sulfur or its compounds are added, or the nitrocompounds used must contain a considerable amount of thiophene derivatives.	Metals of the 2nd to the 8th groups, active silica gel, or Al gel.	I. G. Farbenindustrie A.-G.: E.P. 295,824 (1928). E.P. 297,212 (1928). F.P. 639,557 (1928).
Reduction of nitrobenzene to aniline; nitronaphthalene to aminonaphthalene; nitrophenol to aminophenol; 3-nitropyridine to 3-aminopyridine.	Silica gel, kieselguhr, active charcoal or bleaching earth.	Selden Co. (Jaeger): E.P. 304,640 (1929); refer also to I. G. Farbenindustrie A.-G.: G.P. 458,088 (1927). G.P. 467,638 (1928). E.P. 255,884 (1926).
Reduction of organic compounds: 100 parts nitrobenzene 60 parts water 1 part containing 4 parts Ni by heating a nickel acetate solution with siloxene (oxydisilin).	Catalysts precipitated from metallic salt solutions in the presence of carriers at low or moderate temp. by the action of reducing compounds, SiO <sub>2</sub> .	G.P. 540,327, Kl 120, Dec. 18, 1931; add to G.P. 539,177, Kl 120, Nov. 23, 1931.
Reduction of nitrobenzene to aniline in the gaseous phase.	Co prepared by 24 hrs. heating to 280° from precipitated Co(OH) <sub>2</sub> alone or on asbestos is too active a catalyst; Co-Mn prepared by 2 hrs. heating at 285° of a precipitate obtained from Co(NO <sub>3</sub> ) <sub>2</sub> + KMnO <sub>4</sub> with Na <sub>2</sub> O <sub>2</sub> in the presence of Na <sub>2</sub> CO <sub>3</sub> gives good yields, but	Griffitts and Brown: <i>J. Phys. Chem.</i> , <b>42</b> , 107-111 (1938).

Table 17 (Continued).

Reaction	Catalyst	Observer
	is very sensitive to temp. changes; Co molybdate is a good catalyst, active only at higher temp.; Cr—Co mixed catalysts have no special activity.	

Table 18. Catalytic Reduction of Azo- Compounds.

Reaction	Catalyst	Observer
Reduction of azo- compounds in acid solution occurs faster than for nitro- compounds.	Fe, Cu and Hg.	Lukashewitsch: <i>Zhur. Obshchei Khim.</i> 7, (69) 2209-2225 (1937).
Reduction of azo- and hydrazo- compounds to diamines.	SnCl <sub>2</sub> .	
Reduction of azoxy- compounds to monoamines.		
Reduction of nitro-azo- derivatives.		Brochet: <i>Bull. soc. chim.</i> , 88, 703-707 (1922).

Table 19. Catalytic Reduction of Various Organic Compounds.

Reaction	Catalyst	Observer
Reduction of organic compounds.	Ni(CO) <sub>4</sub> .	Lessig: G.P. 321,938, Kl 12o, Gr 27, June 12, 1920.
Reduction of organic compounds.	Pt and Pd oxides.	Kern, Schriener and Adams: <i>J. Am. Chem. Soc.</i> , 47, 1147-1580 (1925).
Reduction of oxygen-containing organic compounds.	Fe, Cr, or Ni on coal.	Handelsander (Feynald): G.P. 434,211, Cl 12o, Sept. 21, 1926.
Reduction of organic compounds.	Pt oxide-Pt black.	Adams and Garvey: <i>J. Am. Chem. Soc.</i> , 48, 497 (1926).
Selective reduction of furfural-dehyde-acrolein.	Pt oxide-Pt black.	Bray and Adams: F.P. 617,559, Feb. 22, 1927.
Reduction of organic compounds in a methyl alcohol solution, or treated with an ammoniacal substituted organic solute.	Metallic Mg without an activator.	Zedmeister and Kern: G.P. 446,867, Cl 12g, July 13, 1927.
Reduction of Schiff's bases to secondary amines in an acid solution; not suitable for more unstable imino- compounds, such as citral and methylamine, because the hydrolytic action of the acid is greater than the hydrogenation velocity of the acid solution.	Colloidal Pt.	Skita and Keil: <i>Ber.</i> , 61, 1452-1459 (1928).
Reduction of aromatic hydrocarbons.	Pt oxide-Pt black.	Adams and Marshall: <i>J. Am. Chem. Soc.</i> , 50, 1970-1973 (1928).
Reduction of heterocyclic bases: pyridine to piperidine with splitting of the ring to amylamine; pyrrol to pyrrolidine; quinoline to tetrahydroquinoline.	Base-exchanging bodies and active substances; kieselsguhr, silica gel, fuller's earth or active charcoal.	Selden Co. E.P. 304,640 (1929).
Reduction of complex ethers with H <sub>2</sub> ; T. 250°, 220 atm. H <sub>2</sub> pressure; yield of primary alcohols, 80-98% (industrial process).	Cu Chromate (obtained by glowing a mixture of Cu chromate with NH <sub>3</sub> chromate).	Adkins and Connor: <i>J. Am. Chem. Soc.</i> , 53, 1091 (1931).
Reduction of furfural to tetrahydrofurfuryl alcohol; T. 150°; furfural to pentandiolene; T. 200-220°.	Ni carbonate or hydroxide precipitated on silicic acid, silica gel, or fuller's earth.	Shering-Kahlbaum A.-G. (Schoeller and Jordan): G. P. 555,405 (1931).
Reduction of furfural to furfuryl alcohol.	Bleaching earth, silica gel, aluminum gel.	Dupont: E.P. 392,134 (1932).

Table 19 (Continued).

Reaction	Catalyst	Observer
Reduction of furfural with $H_2$ under pressure to furfuryl alcohol or tetrahydrofurfuryl alcohol obtained depending upon the height of pressure and temp.	Hydrogenating catalysts; a mixture of Ni with $MgO$ or kieselguhr.	Quaker Oats Co. (Peters): U.S.P. 1,906,873, May 2, 1933.
Reduction of aryl cyanide, using low fatty acids as solvents; from 3,4,5-trimethoxy-benzoyl and 2 atm., the amino-3,4,5-trimethoxy-acetophenone is obtained.	Metal catalysts of the Pt group, e.g., Pd black.	Kindler and Peschke: G.P. 571,995, Kl 12g, March 4, 1933.
Reduction of Na stearate and Ca formate in cyclohexane (solvent) T. $300^\circ$ ; 200 atm. pressure; theoretical yield, 87%.	Cu on kieselguhr.	Th. Böhme A.-G.: G.P. 576,387 (1933).
Reduction of quinone to oxy-compounds; T. $180^\circ$ .	Through Cu and $Al_2O_3$ promoted Ni contacts.	Yamanaka, Jamada, Kubota and Joshikawa: <i>Bull. Inst. Phys. Chem. Research (Tokyo)</i> , <b>14</b> , 31 (1935).
Reduction of polyoxy-compounds: glycerin to 1,2-dioxypropane; sugars to 1,2-dioxypropane + glycerin; T. $150^\circ$ ; pressure 50 atm.; heated for $2\frac{1}{4}$ hrs.	Ni-Cr on kieselguhr; 150 g. $NiNO_3$ + 12.5 g. Cr sulfate in cold water + 150 g. kieselguhr.	Böhme Fettchemie Gesellschaft m.b.H.: G.P. 634,588 (1936).
Reduction of adrenalon to adrenaline at room temp.; heated 4 hrs.	10% Pd on active charcoal.	Ssergijewskaja and Fedotowa: <i>Ind. org. Chem.</i> <b>2</b> , 96 (1936).
Reduction of chaulmoogric acid chloride (Rosenmund reaction) to unsaturated aldehyde which on further hydrogenation is converted into dihydrochaulmoogric aldehyde; the chaulmoogric acid contains an asymmetric carbon atom; the aldehyde obtained from the right rotating chloride is inactive; Hinegardner (Refer to C. 1933 II 1338) considers racemization as a reason, while Wagner-Yauregg and Voigt account for it by the displacement of the double bond during reduction, so that instead of chaulmoogric aldehyde the optically inactive isochaulmoogric aldehyde is formed; actually by oxidation of the aldehyde with $Ag_2O$ a 47% yield of isochaulmoogric acid is obtained.	Pd- $BaSO_4$ in xylene.	Wagner-Yauregg and Voigt: <i>Ber.</i> , <b>71</b> , 1973-1980 (1938).
Reduction of 2-amino-one-indanol and its derivative isonitroso-indanone with $H_2$ under ordinary or raised temp. and pressure; with Pt, the reduction proceeds up to aminoindanone, being completed with ordinary metals.	Pt group.	Viel and Ahlmann.
Reduction of 5-chlor- derivatives similar to 5-brom-5-alkyl barbituric acid by aqueous alcohol (alcohol is thus converted into acetaldehyde); like the brom-derivatives the alkyl does not markedly influence the reduction velocity, only the isopropyl compounds in both cases are more rapidly reduced than the other homologs; 5-chlor-5-methyl barbituric acid, $C_5H_5O_3N_3Cl$ , is obtained by chlorination of 5-methyl barbituric acid suspended in warm water; 5-chlor-5-propyl barbituric acid, $C_7H_7O_3N_3Cl$ , is obtained from 5-propyl barbituric acid and an excess of $SO_2Cl_2$ in $CHCl_3$ .	Colloidal Pt.	Hughes and Macbeth: <i>J. Chem. Soc.</i> , 1938, 1622-1624.

Table 19 (Continued).

Reaction	Catalyst	Observer
Reduction of carbohydrates containing more C atoms in the molecule than glycerin to form propylene glycol and glycerin from saccharose.	(1) Cu-aluminate heated to a temp. between 750 and 1100°; (2) the catalyst has a cocoa color which is converted into a dark purple up to brown-red by treating with H <sub>2</sub> at 200–350°; this form of the catalyst is the most active; both types are acidic and stable to air.	Association of American Soap and Glycerine Producers, Inc.: E.P. 499,417, Feb. 23, 1939.

## PART IX

## Catalytic Oxidation in Inorganic Chemistry

Table 1. Catalytic Oxidation of Ammonia.

Reaction	Catalyst	Observer
Oxidation of NH <sub>3</sub> by air or O <sub>2</sub> .	MnO <sub>2</sub> , MnO; O <sub>2</sub> transporter; similar action of glowed FeSO <sub>4</sub> while with Pb <sub>2</sub> O <sub>4</sub> , no reaction takes place.	Milner: (1788). Passagez: <i>Ind. chim. Belge</i> , 24, 313–314 (1937) (considers Milner the first discoverer of a catalytic process).
Oxidation of NH <sub>3</sub> to HNO <sub>3</sub> .	Pt.	Kuhlmann: (1839).
Oxidation of NH <sub>3</sub> : 4NH <sub>3</sub> +5O <sub>2</sub> →4NO+6H <sub>2</sub> O.	Manganate, chromate. MnO <sub>2</sub> , FeSO <sub>4</sub> .	C. M. Tessié du Motay: E.P. 491 (1871). Milner: <i>Trans. Roy. Soc. London</i> (A), 79, 300 (1789). Vanquelin, Séguin, Sylvestre: <i>Ann. chim.</i> , 6, 295 (1790). Kuhlmann: <i>Compt. rend.</i> , 7, 1107 (1838); 29, 272–281 (1839). Ostwald, W.: <i>Chem.-Ztg.</i> , 27, 457 (1903).
Oxidation of NH <sub>3</sub> in addition to H <sub>2</sub> O, HNO <sub>3</sub> and N <sub>2</sub> are formed.	MnO <sub>2</sub> . Glowing porcelain.	Bonillon-Lagrange: (1802). Fourcroy: (1800). Davy: (1817). Dobereiner, Dulong and Thénard: (1823); first discoverers of catalytic processes.
Oxidation of NH <sub>3</sub> .	Metals and porous bodies.	Kuhlmann: (1838); essentially the basis of Ostwald's method; this is stated by: Gavelle: <i>Ind. chim. Belge</i> , 24, 160–162 (1937).
Oxidation of NH <sub>3</sub> : NH <sub>3</sub> +2O <sub>2</sub> →HNO <sub>3</sub> +H <sub>2</sub> O	Pt, FeSO <sub>4</sub> .	Ostwald, W.: Swiss P. 25,881 (1902). Brit. P. 8,300 (1902). U.S.P. 858,904 (1902). F.P. 317,544 (1902).
Oxidation of NH <sub>3</sub> : NH <sub>3</sub> +2O <sub>2</sub> →HNO <sub>3</sub> +H <sub>2</sub> O	MnO <sub>2</sub> .	
Oxidation of NH <sub>3</sub> : 4NH <sub>3</sub> +3O <sub>2</sub> →4NO+6H <sub>2</sub> O	ThO <sub>2</sub> +oxides of rare earths.	Franck and Caro: G.P. 224,329 (1907).
Oxidation of NH <sub>3</sub> .	Fe, Co, Ni, as well as their oxides +Bi <sub>2</sub> O <sub>3</sub> ; Fe oxide + W oxide.  Co or Ni or their oxides +Bi <sub>2</sub> O <sub>3</sub> ; Al <sub>2</sub> O <sub>3</sub> +Co <sub>2</sub> O <sub>3</sub> ; BeO+Co <sub>2</sub> O <sub>3</sub> .	Badische Anilin- und Soda Fabrik (Bosch, Mittasch and Beck): G.P. 283,824 (1914).
Oxidation of NH <sub>3</sub> : NH <sub>3</sub> +2O <sub>2</sub> →HNO <sub>3</sub> +H <sub>2</sub> O	Pt or metals of Pt group+layer of Rh.	I. G. Farbenindustrie A.-G.: E.P. 331,728, July 31, 1920.
Oxidation of NH <sub>3</sub> : NH <sub>3</sub> +2O <sub>2</sub> →HNO <sub>3</sub> +H <sub>2</sub> O	V <sub>2</sub> O <sub>5</sub> .	Scalone and Frazer: E.P. 166,285, Aug. 11, 1921.
Oxidation of NH <sub>3</sub> .	MnO <sub>2</sub> +CaO; Co <sub>2</sub> O <sub>3</sub> +Bi <sub>2</sub> O <sub>3</sub> , or Al <sub>2</sub> O <sub>3</sub> , or BeO.	Scott and Leech: <i>Ind. Eng. Chem.</i> , 19, 170 (1927). Piggot: <i>J. Am. Chem. Soc.</i> , 43, 2034 (1921). Kassner: <i>Z. angew. Chem.</i> , 37, 373 (1924).

Table 1 (Continued).

Reaction	Catalyst	Observer
Oxidation of $\text{NH}_3$ .	Pt, Os, or Ni precipitated on fibers.	G.P. 354, 212, K1 12g, June 1, 1922. F.P. 532,343, Feb. 1, 1922.
Oxidation of $\text{NH}_3$ .	Cr silicate impregnated with alkali; V or B silicate impregnated with alkali.	G.P. 298,981, K1 12i, June 16, 1926.
Oxidation of $\text{NH}_3$ .	Polyzeolites; diluted or undiluted $\text{SiO}_2$ containing base exchange bodies stabilized with alkali or alkaline-earth compounds.	G.P. 298,981, K1 12i, June 16, 1926. E.P. 309,582, June 6, 1929.
Oxidation of $\text{NH}_3$ .	Bi and Al+2-10% $\text{Co}_2\text{O}_3$ or other oxides.	Scott and Leech: <i>Ind. Eng. Chem.</i> , <b>19</b> , 170-173 (1927).
Oxidation of $\text{NH}_3$ .	Rhodium.	Duparé, Wenger and Urfer: <i>Hdlv. Chim. Ada</i> , <b>11</b> , 337-348 (1927).
Oxidation of $\text{NH}_3$ .	Pt+5-28% Rh added in the form of an alloy.	Dupont (Davis): U.S.P. 1,706,055, Mar. 19, 1929.
Oxidation of $\text{NH}_3$ .	Pt+1.5% Rh.	Dupont: E.P. 306,382 (1929).
Oxidation of $\text{NH}_3$ .	W silicate with precipitated HCl-Co.	E.P. 309,583 (1929).
Oxidation of $\text{NH}_3$ .	Ca.	Lechewsky and Hofmann: <i>Ber.</i> , <b>62</b> , 2509 (1929).
Oxidation of $\text{NH}_3$ .		Nagel: <i>Z. Elektroch.</i> , <b>36</b> , 754-756 (1930).
Oxidation of $\text{NH}_3$ .	$\text{Fe}_2\text{O}_3 + \text{Bi}_2\text{O}_3$ .	Mittasch: <i>Ibid.</i> , <b>36</b> , 569-580 (1930).
Oxidation of $\text{NH}_3$ .	$\text{Fe}_2\text{O}_3$ (obtained from Fe carbonyl) + $\text{Bi}_2\text{O}_3$ .	I. G. Farbenindustrie A.-G.: F.P. 716,239, Dec. 17, 1931.
Oxidation of $\text{NH}_3$ .	Pt-Rh alloy gauze.	Barnag-Mequin A.-G.: F.P. 686,696, June 29, 1930. F.P. 706,725, June 29, 1931.
Oxidation of $\text{NH}_3$ .	Pt + $\text{WO}_3$ (Mo, Nb or Cr oxides).	I. G. Farbenindustrie A.-G.: F.P. 716, 516, Dec. 22, 1931.
Oxidation of $\text{NH}_3$ .	Pt contact (0.0064-0.01689 pyridine vapor increase yield from 83-99%).	Decarriere and Conder: <i>Chimie &amp; industrie</i> , <b>25</b> , 522-523 (1931).
Oxidation of $\text{NH}_3$ .	Pt net pretreated mechanically by pressing or beating with a hammer.	Yost: F.P. 699,716, Feb. 19, 1931.
Oxidation of $\text{NH}_3$ .	Pt on quartz (to prevent decrease in catalytic activity).	Imperial Chemical Industries, Ltd. (Smyth): E.P. 346,800, May 14, 1931.
Oxidation of $\text{NH}_3$ .	Pt gauze.	Chemical Combustion Corp.: U.S.P. 1,889,549, Nov. 29, 1932.
Oxidation of $\text{NH}_3$ .	Various alloys of Rh with Pt.	F.P. 738,479, Dec. 26, 1932. E.P. 385,859, Jan. 26, 1933.
Oxidation of $\text{NH}_3$ .	85% $\text{Co}_2\text{O}_3$ and 15% $\text{Al}_2\text{O}_3$ (prepared from a mixture of $\text{Co}(\text{NO}_3)_3$ and $\text{Al}_2\text{O}_3$ heated for removal of $\text{H}_2$ ).	Atmospheric Nitrogen Corporation (Fogler): U.S.P. 1,936,936, Nov. 28, 1933.
Oxidation of $\text{NH}_3$ : (1) $\text{NH}_3 \rightarrow \text{N} + \text{H} + \text{H}_2$ (2) $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ (3) $\text{O} + \text{N} \rightarrow \text{NO}$ $\text{NH}_3 + 2\text{O}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O}$ ; chain-like character of the process; OH forms $\text{H}_2\text{O}$ and not $\text{H}_2\text{O}_2$ .	Pt gauze. (1) catalytic splitting. (2) combining of $\text{H}_2$ with $\text{O}_2$ oxidation of $\text{N}_2$ } coupled.	Adaduraw: <i>Zhur. Khim. Prom.</i> , <b>10</b> (2), 37-41 (1933).
Oxidation of $\text{NH}_3$ ; T. 660°; 61% conversion of $\text{NH}_3$ ; 90% $\text{N}_2$ oxides are obtained at higher velocities, 1600ml./min.at 750°.	$\text{SiO}_2$ gel obtained with 10% HCl from water glass and simultaneous addition of $\text{Cr}_2\text{O}_3$ ; introduction of Al into the complex	Adaduraw and Atroschtchenko: <i>Zhur. Priklad. Khim.</i> , <b>6</b> , 1029-1035 (1933).

Table 1 (Continued).

Reaction	Catalyst	Observer
	increases the quality of the catalyst; addition of Co (5.5-6.0%) as $\text{Co}(\text{NO}_2)_2$ improves the physical properties of the catalyst, such as solidity, and also the yield.	
Oxidation of $\text{NH}_3$ .	Be or $\text{Al}_2\text{O}_3$ or their cpds., single or admixed, to Fe or Fe oxide or other Fe cpds.	Sasaki (Shiknen-jo): Jap. P. 98,952, Jan. 9, 1933.
Oxidation of $\text{NH}_3$ .	Pt and a base metal catalyst consisting of $\text{Fe}_2\text{O}_3$ with addition of Bi or Cu.	Maxted: "Catalysis and Its Industrial Application," ch. 14, 15, London, 1933.
Oxidation of $\text{NH}_3$ .	Co salt (precipitated with $(\text{NH}_4)_2\text{CO}_3$ )	Atmospheric Nitrogen Corporation (Bray): U.S.P. 1,918,957, July 18, 1933.
Oxidation of $\text{NH}_3$ .	Catalyst of Pt in which the Rh content decreases in the direction of the gas stream.	Bamag-Meguain A.-G.: Dutch, P. 33,148, July 16, 1934.
Oxidation of $\text{NH}_3$ to $\text{N}_2$ oxides.	Alloy of Pt with 10% Rh; Pd, good catalytic activity in a pure state, as well as in alloys, but becomes breakable in a short time; the use of Pt metals in carriers, also on high melting metals in a gauze form leads to unsatisfactory results.	Handforth and Tilley: <i>Ind. Eng. Chem.</i> , 26, 1287-1292 (1934).
Oxidation of $\text{NH}_3$ ; the assumption that $\text{NH}_3$ is oxidized directly to $\text{HNO}_3$ without intermediate formation of low oxides of $\text{N}_2$ is not acceptable, according to Adadurow and Wainschenker: (Refer to C. 1930 II 1593).	Sn-Ca-SiO <sub>2</sub> .	Tschernajewa: <i>Ukrain. Khem. Zhur.</i> , 9, 92-104 (1934).
Oxidation of $\text{NH}_3$ to $\text{HNO}_3$ .	Fe, Al, Rh, Pt.	
Oxidation of $\text{NH}_3$ .	Metal gauze of Pt or alloys with metals of the Pt group.	Comptoir Général des Métaux Précieux: F.P. 771,524, Oct. 10, 1934.
Oxidation of $\text{NH}_3$ .	Pt + 10% Rh (alloy).	Handforth and Tilley: <i>Ind. Eng. Chem.</i> , 26, 1287-1292 (1934). Bamag-Meguain A.-G.: Dutch P. 33,148, July 16, 1934.
Oxidation of $\text{NH}_3$ .	Pozzuolana earth charged with Pt or Cr; Fe less than Sr less than U less than Mn less than Ce less than Mo less than W less than Cr (increase in activity in this sequence).	Marmier: <i>Compt. rend.</i> , 199, 868-869 (1934); refer also to G.P. 545,427, Kl 12i, Feb. 29, 1932.
Oxidation of $\text{NH}_3$ .	70 parts Co containing impurities + 3.5-5.0 parts $\text{CaCO}_3$ and 1.7-3.5 parts $\text{CaF}_2$ melted and the metal separated from the slag and converted into $\text{Co}_3\text{O}_4$ ; $\text{Co}_3\text{O}_4$ powdered (passes a 100-mesh sieve) mixed with charcoal 17-19% of its weight and the mixture made into a thick paste with a sugar solution.	Atmospheric Nitrogen Corporation (Crittenden): U.S.P. 2,017,683, Oct. 15, 1935.
Oxidation of $\text{NH}_3$ .	Celite sticks (1000-1500°) with mounted wire spirals of Cr steel or Pt metal or Pt-Rh.	Bayerische Stickstoff Werke A.-G.: F.P. 976,205, Jan. 21, 1935.
Oxidation of $\text{NH}_3$ ; (almost complete oxidation—97.5% $\text{NO}$ ; conversion of about 99.2%).	Wire gauze consisting of an alloy of Pt, Rh, Co glowing for 30 min. at 2000° F. and washed with $\text{HCl}$ ; Co content more than Rh content; not more than 4% Co.	Bishop & Co. Platinum Works (Hickey): U.S.P. 2,018,760, Oct. 29, 1935.
Oxidation of $\text{NH}_3$ ; 51% oxidation degree. 34.1% oxidation degree; T. about 750°; 74.1-76.0% oxidation degree.	Cu gauze (destroyed after 18 hrs. use). Brass gauze. Cu plated with Pt. Brass plated with Pt (destroyed after 18 hrs.; not suitable for practical purposes).	Adadurow and Didenko: <i>Ukrain. Khem. Zhur.</i> , 10, 271-276 (1935).



Table 1 (Continued).

Reaction	Catalyst	Observer
Oxidation of $\text{NH}_3$ in a $\text{O}_2$ - $\text{NH}_3$ - $\text{H}_2\text{O}$ mixture, 34% $\text{NO}$ at 750° favorable ratio: $\text{O}_2 : \text{NH}_3 = 2$ (preheating mixture to 100° and using 15% $\text{NH}_3$ ).	Pt-W (Pt losses increased 5-8 times; therefore necessary to find other stable Pt alloys).	Adadurow, and Atroschtchenko Konwissor: <i>Zhur. Priklad Khim.</i> , 9, 1745-1749 (1936).
Oxidation of $\text{NH}_3$ .	Alloys: (1) 92% Pt, 5% Rh and 3% W; gives not only stable (1/3 of the Pt loss against ordinary Pt-Rh gauzes), but also very active gauzes at 900°; gives highly active gauzes but with considerably lower stability than that of Pt-Rh gauze; 0.475 g. Pt loss against 0.15 Pt loss for Pt-Rh gauzes; the admixtures Rh, W, etc., are non-adsorbing $\text{H}_2$ metals and serve to increase the stability of Pt (2) 95% Pt, 2% W and 3% Ag.	Adadurow and Atroschtchenko: <i>Ukrain. Khem. Zhur.</i> , 11, 209-220 (1936); Refer also to Dupont: U.S.P. 1,978,198, Oct. 23, 1934.
Oxidation of $\text{NH}_3$ ; T. up to 750° may be used without corrosion.	Ag plated on Pt nets and Ag-Pt alloy; with increase in Ag content the conversion percentage decreases.	Adadurow, Deutsch and Proskowski: <i>Zhur. Priklad. Khim.</i> , 9, 807-812 (1936).
yields: 72.0% 87.9% 95.7% (T. 935°) air- $\text{NH}_3$ mixtures (10.5% $\text{NH}_3$ ).	Alloys: 50% Ag + 50% Pt 10% Ag + 90% Pt 10% Ag + 80% Pt + 10% Rh	
Oxidation of $\text{NH}_3$ in a mixture with $\text{O}_2$ containing gas.	Pt + 0.5-50% Rh with a surface of pure Pt.	Tilley and Whitehead: Can. P. 368,267, Aug. 24, 1937.
Oxidation of $\text{NH}_3$ .	An alloy consisting of Pt, Rh and W.	Handforth: Can. P. 368,221, Aug. 24, 1937.
Oxidation of $\text{NH}_3$ and simultaneous photoelectric reduction of nitrate to nitrite (faster in alkali than in neutral or acid solution).	Sterilized earth or $\text{Fe}_2\text{O}_3$ .	Kao and Murty: <i>Proc. Nat. Acad. Sci. India</i> , 3, 133-137 (1937).
Oxidation of $\text{NH}_3$ ; *contact time, $1.38 \cdot 10^{-4}$ sec.; yield, 96.2%.	Two catalysts, with respect to their activity, are compared: (1) Pt-Rh-Co alloy [Bishop & Co. (Refer to C. 1936 I 1678)]; (2) Pt-Rh-W alloy [Dupont (Refer to C. 1935 I 1102)]; catalyst (2) shows good results with regard to stability; Rh may be replaced by Ag in Pt and W alloy; good results obtained with an alloy consisting of 95% Pt, 2% W and 3% Ag.*	Adadurow: <i>Zhur. Khim. Prom.</i> , 14, 917-924 (1937).
Oxidation of $\text{NH}_3$ . $\text{NH}_3 + \text{CH}_4 + 1-1/2\text{O}_2 \rightarrow \text{HCN} + 3\text{H}_2\text{O} + 114,900 \text{ cal.}$	Pt; as intermediate product not atoms, but $\text{CH}_3\text{NH}_2$ (from $\text{H}_2\text{C} : \text{NH}$ obtained by reduction of $\text{HCN}$ to $\text{NH}_3 + \text{CH}_4$ ).	Andrussow: <i>Ber.</i> , 71, 776-778 (1938).
Oxidation of $\text{NH}_3$ .	$\text{Al}_2\text{O}_3$ , $\text{MgO}$ or $\text{ZrO}_2$ .	
Oxidation of $\text{NH}_3$ under small pressures; (1) pure $\text{NH}_3$ passed over glowing Pt produces a small decomposition with hydrazine formation; with increasing $\text{O}_2$ conc., $\text{NH}_3$ is used up faster, while $\text{N}_2\text{H}_4$ formation is simultaneously depressed; (2) with increasing $\text{O}_2$ content in the initial gas, the yield of $\text{NH}_4\text{OH}$ and $\text{HNO}_2$ with respect to the decomposed $\text{NH}_3$ increases; (3) as a single non-condensed gas $\text{N}_2$ is formed; neither N oxides nor $\text{H}_2$ are formed; the $\text{NO}$ formed in the industrial process under ordinary pressure is a	Glowed Pt.	Bodenstein, Büttner and Krauss: (Refer to C. 1935 II 2624).

Table 1 (Continued).

Reaction	Catalyst	Observer
secondary product from $\text{HN}_2\text{OH}$ and $\text{HNO}_2$ ; (4) with increasing temp., the use of $\text{NH}_3$ for all mixture ratios slowly increases; slightly faster is increase of the formation of $\text{NH}_2\text{OH}$ and $\text{HNO}_2$ .		
Oxidation of $\text{NH}_3$ ; the place where $\text{HNO}_2$ is formed is not only the catalyst surface, but the gaseous space as well; for the formation of $\text{N}_2$ is assumed the following reaction on the catalyst: $\text{NH}_2\text{OH} + \text{HNO} \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ ; it is deduced from the small amount of hydrazine formed that $\text{NH}_2\text{OH}$ is not formed first from $\text{NH} + \text{H}_2\text{O}$ , at the wall of the container, and that the primary reaction product is not the assumed $\text{NH}$ radical.	Glowed Pt.	Krauss: <i>Z. physik. Chem. (B)</i> , <b>39</b> , 83-100 (1938).
Oxidation of ammonia with $\text{O}_2$ .	$\text{Co}_2\text{O}_3$ which contains less than 0.01 P calculated as $\text{P}_2\text{O}_5$ per 100 Co ( $\text{Co}_2\text{O}_3$ is obtained by precipitation of Co from a $\text{Co}(\text{NO}_2)_2$ solution with $\text{NH}_3$ and heating the obtained precipitate).	Solvay Process Co. (Atmospheric Nitrogen Corporation (Bray)): Can. P. 371,771 and 371,772, Feb. 8, 1938).
Oxidation of $\text{NH}_3$ to $\text{NO}$ ; constant T. $700^\circ$ ; yield, 96-98%.	Three kinds Pt wires: (1) Pt alloy with high catalytic activity and high yields; (2) wires so active that they convert gases without preliminary heating; and (3) wires of pure Pt; wires (1) consist partially of Pt-Rh and otherwise of Pt-Ir alloys; the Rh content should be high, the Ir content low; the life-time of such gauzes is estimated to be 24 months; losses of Pt amount to about 0.232 g.	Lonza Elektrizitätswerke und Chemische Fabriken A.-G. (Gampel und Basel): Swiss P. 197,271, July 16, 1938.
Oxidation of $\text{NH}_3$ ; likewise hydrogenation and dehydrogenation of hydrocarbons or hydrogenation of alcohols or other gas reactions.	The catalyst is an alloy containing more than 50% Pt and Rh beside at least one metal: Os, Ir, Rh, Pd, W, V, Zr, or Th in the form of gauze spiral or perforated plate; if W or V is used these are recrystallized by heat; such catalysts have good mechanical properties.	I. G. Farbenindustrie, A.-G.: E.P. 491,143, Sept. 22, 1938.
Oxidation of $\text{NH}_3$ ; the yield increases from about 90% to about 94-96%.	An alloy containing Pt metals which have been recrystallized to the form of a distinct grain; preferably the alloy consists of Pt with 2% Ru, likewise 1% Ru more, heated for several hours to $1000^\circ$ .	I. G. Farbenindustrie A.-G.: Swiss P. 198, 702, Oct. 1, 1938; refer also to Belg. P. 422,398, Sept. 13, 1935 (Refer to C. 1938 II 1456), and E.P. 491,143, Jan. 26, 1937 (Refer to C. 1938 II 4111).
Oxidation of $\text{NH}_3$ ; for oxidation scheme refer to C. 1930 II 2736.	Pt and oxide catalysts.	Nagel: <i>Z. physik. Chem. (B)</i> , <b>41</b> , 71-74 (1938).

Table 2. Catalytic Oxidation of Sulfur Dioxide or Sulfurous Acid to Sulfuric Acid.

Reaction	Catalyst	Observer
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ by the $\text{H}_2\text{SO}_4$ contact process.	Oxides of $\text{N}_2$ .	Clément and Désormes: (1806).
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ by the $\text{H}_2\text{SO}_4$ contact process. $\text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$	Pt; Pt on asbestos.	Phillips: E.P. 6,096 (1831). Petrie: E.P. 590 (1852).
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ .	Oxides of Fe, Cr and Cu instead of Pt.	Wöhler and Mahla: (1852).

Table 2 (Continued).

Reaction	Catalyst	Observer
Oxidation of SO <sub>2</sub> to H <sub>2</sub> SO <sub>4</sub> .	Pt on carriers; Pt on solid salts.	Winkler: G.P. 4,566 (1878). Grillo and Schroeder: G.P. 102,244 (1898).
Oxidation of SO <sub>2</sub> to H <sub>2</sub> SO <sub>4</sub> .	WO <sub>3</sub> less active than V <sub>2</sub> O <sub>5</sub> (intermediate product, vanadyl sulfate).	Neumann and Goebel: <i>Z. Elektroch.</i> , 34, 734-740 (1928). Neumann, Pauzner and Goebel: <i>Ibid.</i> , 34, 696-707 (1928).
Oxidation of SO <sub>2</sub> to H <sub>2</sub> SO <sub>4</sub> .	Vanadium silicate; complex V cpds. of the type of base-exchanging bodies (more active and stable toward high temp. than Pt catalyst).	Jaeger: <i>Ind. Eng. Chem.</i> , 21, 627-632 (1929).
Oxidation of SO <sub>2</sub> to H <sub>2</sub> SO <sub>4</sub> .	Colloidal Pt impregnated in small amounts on silica gel; (Pt obtained by reduction of PtCl <sub>4</sub> ); higher activity found for colloidal Pt brought upon previously prepared gel.	Charmadarjan and Dachnjuk: <i>Ukrain. Khim. Zhur.</i> , 8 (S.P.), 36-43 (1933).
Oxidation of SO <sub>2</sub> to H <sub>2</sub> SO <sub>4</sub> .	Fe surface with a Pt layer; cathodic dispersion of Pt on Fe; Pt vapors condensed on asbestos in vacuum (the same activity as ordinary platinized asbestos).	Dankow, Joffe, Kotschetkow and Perewesentzew: <i>J. Russ. Phys.-Chem. Soc.</i> , 4, 334-342 (1933).
Oxidation of SO <sub>2</sub> to H <sub>2</sub> SO <sub>4</sub> .	8 parts Te <sub>2</sub> O <sub>3</sub> in 200 vol. H <sub>2</sub> O + V <sub>2</sub> O <sub>5</sub> on kieselguhr or diatomaceous earth or celite pieces (250 parts by volume silo-cell. C <sub>22</sub> ); Te <sub>2</sub> O <sub>3</sub> : Ag <sub>2</sub> O : V <sub>2</sub> O <sub>5</sub> = 1/4 : 1 : 1.	Selden (Fiedler and Jaeger): U.S.P. 1,945,267, Jan. 30, (1934).
Oxidation of SO <sub>2</sub> to H <sub>2</sub> SO <sub>4</sub> .	C-containing pyrite + V catalyst.	Boreskow and Ssokolowa: <i>Zhur. Khim. Prom.</i> , 6, 18-22 (1934).
Oxidation of SO <sub>2</sub> to H <sub>2</sub> SO <sub>4</sub> by the H <sub>2</sub> SO <sub>4</sub> contact process; T. 260-540°.	Cr <sub>2</sub> O <sub>3</sub> , SnO <sub>2</sub> (Cr nitrate should be used instead of Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ); 2SiO <sub>2</sub> , Cr <sub>2</sub> O <sub>3</sub> , Na <sub>2</sub> O + H <sub>2</sub> O (zeolite structure) 180 cc. of a 0.03 g./cm. SiO <sub>2</sub> containing Na silicate solution (alkalinity, 0.3955N) heated with 60 cc. 4.8085N NaOH at 70° to which is gradually added 86.5 cc. Cr nitrate (0.079 g. Cr <sub>2</sub> O <sub>3</sub> per cc. acidity 3.024N) the zeolite precipitates out at 65-70° with stirring for 4 days, dried (after washing) in a stream of air at 60-70° and finally at 100°.	Adadurow: <i>Ibid.</i> , 11, 53-55 (1934). Adadurow: G.P. 316,858 (1920).
Oxidation of SO <sub>2</sub> to H <sub>2</sub> SO <sub>4</sub> .	V catalyst mass on K <sub>2</sub> O-VO <sub>2</sub> -SiO <sub>2</sub> .	Metall-A.-G. (Siecke and Koolmann): G.P. 610,448, Kl 12, March 13, 1935. G.P. 610,449, Kl 12, March 11, 1935.
Oxidation of SO <sub>2</sub> to H <sub>2</sub> SO <sub>4</sub> .	Commercial Ca vanadate; alkali vanadate better than SiO <sub>2</sub> + V <sub>2</sub> O <sub>5</sub> .	Neumann: <i>Z. Elektroch.</i> , 41, 589-593 (1935).
Oxidation of SO <sub>2</sub> with H <sub>2</sub> O under pressure; T. 175-230°. 3SO <sub>2</sub> + 2H <sub>2</sub> O → 2H <sub>2</sub> SO <sub>4</sub> + S (NH <sub>4</sub> ) <sub>2</sub> SO <sub>3</sub> + 2NH <sub>4</sub> HSO <sub>3</sub> → 2(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + S + H <sub>2</sub> O for aqueous solution SO <sub>2</sub> the highest limit is 10% H <sub>2</sub> SO <sub>4</sub> .	H <sup>+</sup> slows down strongly the obtaining of conc. H <sub>2</sub> SO <sub>4</sub> ; S, Se and aqueous solution of (NH <sub>4</sub> ) <sub>2</sub> S and H <sub>2</sub> S.	Kusmin and Plotnikow: <i>Zhur. Khim. Prom.</i> , 12, 571-580 (1935).
Oxidation of SO <sub>2</sub> in solution of bivalent Mn salts (strong H <sub>2</sub> SO <sub>4</sub> may be obtained from flue gases by using this method).	Mn <sup>II</sup> salts by oxidation of SO <sub>2</sub> and Mn <sup>III</sup> ; a complex of Mn <sup>II</sup> with SO <sub>2</sub> is formed; a part of Mn <sup>II</sup> with H <sub>2</sub> SO <sub>4</sub> gives a stable complex ion which cannot be regenerated (like Mn <sup>III</sup> , SO <sub>2</sub> complex which is regenerated by reaction with SO <sub>2</sub> ); to maintain the velocity of the process, a new amount of Mn salt must be introduced—O <sub>2</sub> may be used;	Grodowski: <i>Zhur. Fiz. Khim.</i> , 6, 478-495 (1935); 6, 496-510 (1935).

Table 2 (Continued).

Reaction	Catalyst	Observer
	O <sub>2</sub> accelerates oxidation of Mn-SO <sub>2</sub> complexes and causes direct oxidation of Mn <sup>++</sup> .	
Oxidation of SO <sub>2</sub> to H <sub>2</sub> SO <sub>4</sub> ; T. 475-550°; highest yield of SO <sub>3</sub> , 98.4%, reached at 440°.	Salts of Ag and Na vanadate, best catalytic activity; K metavanadate, medium activity, and Te metavanadate, smallest activity; Na <sub>2</sub> O · 3V <sub>2</sub> O <sub>5</sub> ; catalytic action depends on the binding state of V <sub>2</sub> O <sub>5</sub> ; 3SnO <sub>2</sub> · V <sub>2</sub> O <sub>5</sub> · Na <sub>2</sub> O is less active than NaVO <sub>3</sub> ; 2Na <sub>2</sub> O · 3MoO <sub>3</sub> · V <sub>2</sub> O <sub>5</sub> is more active than NaVO <sub>3</sub> ; Na-Mo-V contact suitable for technical application.	Causeri and Vajna de Pava: <i>Ann. chim. applicata</i> , 26, 560-570 (1936). Kröger and Iwanowski: <i>Z. Elektroch.</i> , 41, 821-34 (1935). Neumann: (Refer to C. 1936 I 2165).
Oxidation of SO <sub>2</sub> by O <sub>2</sub> ; T. 0-20°; method to be used in the purification of flue gases for removal of SO <sub>2</sub> with simultaneous formation of H <sub>2</sub> SO <sub>4</sub> .	MnSO <sub>4</sub> in the presence of phenol poison (phenol decreases the yield of H <sub>2</sub> SO <sub>4</sub> simultaneously increasing the formation of dithionic acids).	Kashtanow and Ryschow: <i>Zhur. Obshchei Khim.</i> , 6 (68), 549-554 (1936).
Oxidation of SO <sub>2</sub> to H <sub>2</sub> SO <sub>4</sub> ; the gas mixture should contain at least 10% SO <sub>2</sub> and 5% O <sub>2</sub> and at most 70% inert gases; more than 80% SO <sub>2</sub> is converted into SO <sub>3</sub> ; SO <sub>3</sub> is condensed or adsorbed and the unconverted SO <sub>2</sub> led back into the process.	Heated catalyst.	Canadian Industries, Ltd. (Tyrer and Clark): Can. P. 365,631, April 27, 1937.
Oxidation of SO <sub>2</sub> to H <sub>2</sub> SO <sub>4</sub> ; T. 400-425°; temp. coefficient calculated is 1.23; T. 425-450°; temp. coefficient calculated is 1.19; T. 400-450°; temp. coefficient calculated is 1.17; the optimum temp. <i>t</i> for a conversion degree <i>x</i> with least amount of catalyst is calculated from an equation which gives the value <i>x</i> = 98%, <i>t</i> = 440° and <i>x</i> = 94%, <i>t</i> = 496° and <i>x</i> = 90%, <i>t</i> = 526°.	8.26% V <sub>2</sub> O <sub>5</sub> activated with K <sub>2</sub> O.	Matsui and Kiyoura: <i>J. Soc. Chem. Ind. Japan (Suppl.)</i> , 40, 465B-467B (1937).
Oxidation of SO <sub>2</sub> to H <sub>2</sub> SO <sub>4</sub> ; T. 400°; composition of gases: 7% SO <sub>2</sub> , 19.5% O <sub>2</sub> , 73.5% N <sub>2</sub> ; yield of H <sub>2</sub> SO <sub>4</sub> , 99%.	Pt catalyst 0.01-0.5% by weight (10% Pt may be replaced by Rh); as activators are used Fe <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> , MgO + As <sub>2</sub> O <sub>3</sub> , 1% by weight with respect to the weight of the Pt; as result of ultra-filter structure of the high content of Si carrier, a high activity of the catalyst is attained, also smaller content of Pt necessary; it is non-poisonous toward As cpds. and simple to prepare.	American Platinum Works: Aust. P. 153,795, July 11, 1938; refer to C. 1937, 1936. F.P. 803,746, March 17, 1936. (Refer to C. 1937 I 1223-24).
H <sub>2</sub> SO <sub>4</sub> is prepared by the use of special equipment; the gases streaming through the layers of the catalyst in changing direction are cooled indirectly in special heat exchangers, e.g., by cold air; the streaming velocity in one direction should be greater than that in the opposite direction; the walls of the contact oven are built into filters to free the gases from dust and other impurities.	Catalyst in layers.	American Cyanamid and Chemical Corporation (Clark): Can. P. 375,737, Aug. 13, 1938.
Oxidation of 5% SO <sub>2</sub> -containing gas; T. 451° (optimum); yield, 96%.	Vanadium.	Tschernobajew: <i>Zhur. Khim. Prom.</i> , 15 (Nr. 9), 11-13 (1938); (Refer to C. 1937 II 1055).
H <sub>2</sub> SO <sub>4</sub> process, high conc. gases, 10-14% SO <sub>2</sub> + 90-96% O <sub>2</sub> , or 30% SO <sub>2</sub> + 70% O <sub>2</sub> ; T. 420-450°; yield, 91-100%; it is recommended to lower the high reaction temp. (600°) for these concentrations by adding por-	Thin layers.	Bachalard: <i>Ind. chim. belge</i> , 26, 154-57 (1939).

Table 2 (Continued).

Reaction	Catalyst	Observer
tions of cold gas with increasing content of $\text{SO}_2$ , e.g., 9–10% $\rightarrow$ 25% $\rightarrow$ 30%.		
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ ; sulfur is burned with dried air to $\text{SO}_2$ , the latter cooled, then filtered, heated to the contact temp., heat exchangers with contact outlet gases and catalyzed; air is dried by means of activated $\text{Al}_2\text{O}_3$ or silica gel; regeneration of the drying agent follows by means of hot air which is heated with $\text{SO}_2$ gases in the heat exchanger.		Dupont: U.S.P. 2,163,371, June 20, 1939.
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ .	V catalyst is prepared by substituting metavanadate and K silicate with an acid solution of Ba-Sb or Fe chloride and drying the precipitated sediment after filtering off.	Kagan, Schmarjan, Schokin and Itkina: Russ. P. '52,798, March 31, 1938.
Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ with $\text{O}_2$ activated by a mixture of $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$ ; the process is carried out continuously, starting with a mixture of $\text{SO}_2$ , $\text{Cl}_2$ and $\text{O}_2$ .	$\text{Cl}_2$ obtained by oxidation of $\text{HCl}$ .	Soc. Internationale des Industries Chimiques et Dérivés Soc. An.: F.P. 834,124, Nov. 14, 1938.

Table 3. Catalytic Oxidation of Sulfur Dioxide.

Reaction	Catalyst	Observer
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Nitroso- group containing gases.	Clément and Désormes: (1806).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Pt.	Philippe: B.P. 6,096 (1831).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ . $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ .	$\text{CuO}$ , as well as $\text{Fe}_2\text{O}_3$ or $\text{Cr}_2\text{O}_3$ .	Dobereiner: Ann., 2, 343 (1832). Magnus: Pogg's Ann., 24, 610 (1832).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Pt on asbestos; Pt on carriers.	Petrie: B.P. 590 (1852)
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{Fe}_2\text{O}_3$ .	Robb: B.P. 731 (1853). B.P. 788 (1853).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ by air.	Pt on carriers.	Winkler: (1875). Winkler: G.P. 4,566 (1878).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ by contact process with gases from roasting.	Pt.	Badische Anilin- und Soda Fabrik (Knietzsch): (1890).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Pt on solid salts, such as $\text{CuO}$ , $\text{Fe}_2\text{O}_3$ , or $\text{Cr}_2\text{O}_3$ . Pt on $(\text{CuO} + \text{Cr}_2\text{O}_3)$ .	Grillo and Schroeder: G.P. 102,244 (1898).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Fe oxide instead of Pt.	Verein Chemische Fabriken von Mannheim (Hasenbach and Clément): G.P. 107, 995 (1898).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{V}_2\text{O}_5$ .	deHaen: G.P. 128, 616 (1900).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{Fe}_2\text{O}_3$ and Pt. $\text{Fe}_2\text{O}_3$ , $\text{CuO}$ , $\text{Cr}_2\text{O}_3$ .	Verein Chemische Fabriken von Mannheim (Hasenbach and Clément): G.P. 107,995 (1898). Badische Anilin- und Soda Fabrik: G.P. 140,353 (1901).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{FeSO}_4$ on burned Fe pyrites.	Farbenfabrik vorm Meister Lucius Brüning: G.P. 139,354 (1902).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Sulfates of rare earths.	Höbbling and Diets: G.P. 142,144 (1902).

Table 3 (Continued).

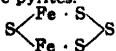
Reaction	Catalyst	Observer
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Ignited Fe pyrites. 	
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ . $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ .	$\text{CuO}$ , as well as $\text{Fe}_2\text{O}_3$ or $\text{Cr}_2\text{O}_3$ .	Bodenstein and Fink: <i>Z. physik. Chem.</i> , <b>60</b> , 1 (1907). Taylor: <i>Can. Chem. Met.</i> , <b>10</b> , 38 (1926). Neumann: <i>Z. Elektroch.</i> , <b>34</b> , 734 (1928).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{AgVO}_3$ .	Bayer: G.P. 280,960 (1912).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Activated $\text{V}_2\text{O}_5$ .	Badische Anilin- und Soda Fabrik: G.P. 291,792 (1913). G.P. 128,616 (1900). Swiss P. 71,326 (1913).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Pt on $\text{Fe}_2\text{O}_3 \cdot \text{CuO}$ as carrier.	Badische Anilin- und Soda Fabrik: G.P. 291,792 (1913). Swiss P. 71,326 (1913).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{Cr}_2\text{O}_3$ + oxide.	Ellis: U.S.P. 1,204,141 (1916).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Ni boron silicate.	G.P. 298,981, Kl 12i, June 16, 1920.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{V}_2\text{O}_5$ .	Scalione and Frazer: E.P. 166,285, Aug. 11, 1921.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Pt, Os or Ni on fibers.	G.P. 354,212, Kl 12g, June 1, 1922. F.P. 532,343, Feb. 1, 1922.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Catalysts containing Pt.	G.P. 440,338, Kl 12i, Dec. 6, 1927.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{MgSO}_4$ or porous ceramics impregnated with a Pt solution.	Astner: E.P. 265,938, April 6, 1927.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Many component zeolites prepared from silicates plus one or more metals or salts.	Selden Co.: E.P. 290,316, June 14, 1928.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Double zeolite + catalyst.	Selden Co.: E.P. 296,048, Oct. 17, 1928.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ ; yield, 97.0–99.4%.	$\text{AgVO}_3$ ; complex vanadium silicate.	Adadurow and Boreskow: <i>Zhur. Khim. Prom.</i> , <b>6</b> , 805–807 (1928).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{V}_2\text{O}_5$ , $\text{MoO}_3$ , $\text{WO}_3$ , $\text{Cr}_2\text{O}_3$ , $\text{Mn}_2\text{O}_3$ , $\text{Mn}_2\text{O}_7$ , $\text{WO}_3$ on zeolites.	U.S.P. 1,657,753, Jan. 31, 1928.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{Li}_2\text{CO}_3$ less than $\text{Na}_2\text{CO}_3$ less than $\text{K}_2\text{CO}_3$ ; $\text{Na}_2\text{SiF}_6$ excellent; $\text{Na}_2\text{WO}_4$ , $\text{B}_2\text{O}_3$ and $\text{P}_2\text{O}_5$ moderate action; 1% causes rapid conversion.	Niwenburg and Nooijer: <i>Rec. trav. chim.</i> , <b>47</b> , 627–634 (1928).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Platinized silicic acid gel.	Holmes, Ramsay and Elder: <i>Ind. Eng. Chem.</i> , <b>21</b> , 850–853 (1929).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	V compounds.	Waeser: <i>Metallbörse</i> , <b>19</b> , 1350–1351, 1406–1409 (1929).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{V}_2\text{O}_5 + \text{SnO}_2$ .	Poljakow: <i>Zhur. Fiz. Khim.</i> , <b>2</b> , 147–150 (1931).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Rhenium oxide or rhenium alloy.	Siemens and Halske: Swiss P. 146,845, July 16, 1931; F.P. 682,244.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$8\text{SiO}_2 \cdot 2\text{SnO}_3$ , $\text{V}_2\text{O}_5$ , $\text{K}_2\text{O}$ , $\text{BaO}$ .	Boreskow and Pligunow: <i>Zhur. Priklad. Khim.</i> , <b>6</b> , 785–796 (1933).

Table 3 (Continued).

Reaction	Catalyst	Observer
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ ; yield 97-98%	Catalyst obtained through direct precipitation of water glass solution with Mn salts ( $450^\circ$ ).	Charmadarjan and Brodowitsch: <i>Ukrain. Khim. Zhur.</i> , (Se. Part) —, 58-65 (1933).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Oxides of $\text{N}_2 + \text{V}_2\text{O}_5$ .	Maxted: "Catalysis and Its Industrial Application," ch. 14, 15, 1933.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Ca vanadate (treated with potash solution under $\text{CO}_2$ , substituted by potassium silicate and then by $\text{BaCl}_2$ ).	Schmarijan, Sechokin, Kogan and Podrabinek: Russ. P. 33,958, Jan. 31, 1934.
Oxidation of $\text{SO}_2$ by $\text{O}_2$ and $\text{O}_2$ -containing gases in two steps.	V contact mass.	General Chemical Co. (Merrian): U.S.P. 1,965,963 (1934).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$2\text{SiO}_2 \cdot \text{Cr}_2\text{O}_3 \cdot \text{Na}_2\text{O}$ .	Adaduraw: <i>Zhur. Khim. Prom.</i> , 11, 53-55 (1934); refer also to Vortmann: G.P. 316,858, Kl 12i Gr 24, Aug. 28, 1918.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{BaO} + \text{V}_2\text{O}_5$ ; $\text{CaO} + \text{V}_2\text{O}_5$ ; $\text{BaO}$ more active than $\text{CaO}$ .	Maklakow and Archipowa: <i>Khimstroj</i> , 6, 318-321 (1934).
Oxidation of $\text{SO}_2$ by $\text{O}_2$ of air.	Bivalent Mn (velocity of the reaction increases with an increase in the acidity of the solution); $\text{H}_2\text{SO}_4$ poisons the $\text{MnSO}_4$ catalyst; a 20% $\text{H}_2\text{SO}_4$ solution stops the reaction completely.	Kaschtanow and Ryshow: <i>Zhur. Khim. Prom.</i> , 13, 1225-1228 (1936). Afanasjew: Russ. P. 42,055, March 31, 1935.
Oxidation of $\text{SO}_2$ by $\text{O}_2$ to $\text{SO}_3$ .	The mixture of $\text{PtO} + \text{PtO}_2$ is prepared by heating finely divided Pt to $410^\circ$ under 170 atm. $\text{O}_2$ pressure (the mixture contains 30% $\text{PtO}$ ).	Lafitte and Grandadam: <i>Congr. chim. ind., 15th Congr., Brussels</i> , 15 (I), 319-323 (1935).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ ; T. $450^\circ$ ; activation heat of mixed catalysts, 19,000-22,000 cal.; activation heat of Pt catalysts (IG), 17,000 cal.	$\text{BaO} - \text{V}_2\text{O}_5$ , also $\text{CaO} - \text{V}_2\text{O}_5$ ; Pt catalysts (I. G. Farbenindustrie A.-G.).	Boresskow and Pligunow: <i>Zhur. Khim. Prom.</i> , 13, 422-423 (1936).
Oxidation of $\text{SO}_2$ gases containing F and As cpds. freed from impurities by the addition of $\text{SiO}_2$ and heating at $600^\circ \text{F}$ .	Vanadium.	American Cyanamid and Chemical Corporation (Clark): U.S.P. 2,028,739, Jan. 28, 1936; refer also to U.S.P. 2,028,733, Jan. 21, 1936.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ ; precipitate mixed with $\text{Si}(\text{OH})_4 + \text{NH}_4\text{VO}_3$ and $\text{K}_2\text{SO}_4$ ; ratio of V : K = 1 : 2- $\frac{1}{2}$ up to 1 : 3- $\frac{1}{2}$ .	$\text{NH}_4\text{VO}_3$ , $\text{KNO}_3$ , V sulfate impregnated with gelatinous $\text{Si}(\text{OH})_4$ ; 10-20 parts $\text{SiO}_2$ to 1 part V.	Calco Chemical Co., Inc. (Beardsley): U.S.P. 2,042,922, June 2, 1936. U.S.P. 2,027,316, Jan. 7, 1936.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{SiO}_2$ gel impregnated with Na, K vanadate solution and dried at $120^\circ$ ; precipitate of Ag, Ba, Al, Pb, Sn and Mn cpds. with $\text{NaVO}_3$ upon $\text{SiO}_2$ gel; activators from the left half of the Periodic System act more strongly than those from the right half.	Ken-ichi Oda, Waka and Kohima: <i>J. Chem. Soc. Japan (Suppl.)</i> , 39, 471B (1936).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Diatomaceous earth containing about 90% $\text{SiO}_2$ , 4% $\text{Al}_2\text{O}_3$ and a small amount of Fe, CaO, MgO is impregnated with $\text{NaVO}_3$ or $\text{NH}_4\text{VO}_3$ (27.2 g.); most of the impregnated substances should remain on the surface; as accelerators may be applied Bi, Cd, Pb, Ag, Be or alkali or alkaline earths; instead of diatomaceous earth kieselguhr may be used; as impregnating solution 76 g. $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ or equivalent salts of Cu, Co, Ni or their mixtures may serve.	American Cyanamid and Chemical Corporation (Jaeger): U.S.P. 2,029,530, Feb. 4, 1936. U.S.P. 2,029,551, Feb. 4, 1936.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	Fe oxide.	Neumann and Heintke: <i>Z. Elektroch.</i> , 43, 246 (1937).

Table 3 (Continued).

Reaction	Catalyst	Observer
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ .	$\text{SiO}_2$ is brought to a pasty form with a solution containing alkali or alkaline-earth phosphate; the mass is molded to catalyst body and impregnated with $\text{KVO}_3$ .	Metallgesellschaft A.-G.: (von Girssewald, Siecke and Wohlwill); G.P. 649,401, Kl 12g, Aug. 23, 1937.
Oxidation of $\text{SO}_2$ by $\text{O}_2$ to $\text{SO}_3$ .	Contact chambers filled with suitable catalysts.	Dupont (Zeisberg); U.S.P. 2,075,075, March 30, 1937.
Oxidation of $\text{SO}_2$ by $\text{O}_3$ ; $\text{O}_3$ is introduced directly or indirectly with flue gases; a semi-industrial process.		Kaschtanow: <i>Zhur. Khim. Prom.</i> , 14, 365-369 (1937). Kaschtanow: (Refer to C. 1937 II 922).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ ; T. $400^\circ$ , yield 18-29% T. $500^\circ$ , yield 29-39% T. $600^\circ$ , yield 37-45% T. $650^\circ$ , yield 47-60%	Mixture of 77% $\text{TiO}_2$ , 21.7% $\text{Nb}_2\text{O}_5$ and 1.2% $\text{Ta}_2\text{O}_5$ (obtained from loparite mineral); this catalyst is very stable to poisons; it is assumed that $\text{TiO}_2$ is strongly activated by $\text{Nb}_2\text{O}_5$ and $\text{Ta}_2\text{O}_5$ .	Platonow and Spewakowa: <i>Zhur. Priklad. Khim.</i> , 10, 1537-1540 (1937).
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ ; T. $400^\circ$ , yield 9.4% T. $600^\circ$ , yield 21.4% T. $650^\circ$ , yield 30.0%	$\text{TiO}_2$ alone.	Neumann and Goebel: <i>Z. Elektroch.</i> , 34, 734-740 (1928); (Refer to C. 1929 I 839).
Oxidation of $\text{SO}_2$ by $\text{O}_2$ to $\text{SO}_3$ .	Carbonyls: volatile compounds of elements of the 8th group of the Periodic System; $\text{Fe}(\text{CO})_5$ , $\text{Fe}(\text{CO})_9$ , $\text{Fe}(\text{CO})_8$ , $\text{Ni}(\text{CO})_4$	Gesellschaft für Linde's Eis Maschinen A.-G. (Schuftan): G.P. 660,734, Kl 12i, June 1, 1938.
Oxidation of $\text{SO}_2$ to $\text{SO}_3$ ; gases containing more than 20% $\text{SO}_2$ and the required amount of $\text{O}_2$ ; in the catalyzed gases the partial pressure of $\text{SO}_2$ is greater than 200 mm. Hg; $\text{SO}_3$ may be condensed directly; the gases may be circulated many times over the catalysts connected in a series; gases up to 66% $\text{SO}_2$ can be worked out, especially those originating from reduction of $\text{CaSO}_4$ or from the combustion of S with $\text{O}_2$ or air enriched with $\text{O}_2$ .	Pt or V.	Soc. des Produits Azotes; F.P. 833,634, Oct. 26, 1938.

Table 4. Catalytic Oxidation of Sulfurous Acid and Ammonium Sulfite.

Reaction	Catalyst	Observer
Oxidation of $\text{H}_2\text{SO}_3$ by air; the oxidation velocity in the presence of the catalyst for small conc. of $\text{H}_2\text{SO}_3$ is 7-8 times greater than the velocity of the non-catalytic oxidation.	0.01% $\text{MnSO}_4$ .	Wassiljew, Kaschtanow and Rastorskaja: <i>Acta Physicochim. U.R.S.S.</i> , 3, 413-434 (1935).
Oxidation of crystalline $(\text{NH}_4)_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$ with $\text{O}_2$ and with air; by using air the same oxidation degree is reached in 5-fold time as with $\text{O}_2$ .	Nitrates of Ni, Mn, Fe, Co and Cu; the function of the catalyst is to increase the $\text{O}_2$ pressure.	Sernagiotto and Casavecelria: <i>Chimica e industria</i> , 17, 220-223 (1935); refer also to Haber and Bram: <i>Z. physik. Chem.</i> , 35, 84 (1900).

Table 5. Catalytic Oxidation of Hydrogen Sulfide.

Reaction	Catalyst	Observer
Oxidation of $\text{H}_2\text{S}$ to S.		Chance and Claus: (1885).
Oxidation of $\text{H}_2\text{S}$ to S; $\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{S} + \text{H}_2\text{O}$ .	Active charcoal.	Schumacher: G.P. 331,287 (1917).
Oxidation of $\text{H}_2\text{S}$ to S; $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$ .	Active charcoal + traces of $\text{NH}_3$ .	Badische Anilin- und Soda Fabrik G.P. 374,358 (1919). Bayer: G.P. 303,862 (1917) Engelhardt: <i>Z. angew. Chem.</i> , 34, 219 (1921). Hoffmann: <i>Chem. App.</i> , 16, 61 (1929).



Table 5 (Continued).

Reaction	Catalyst	Observer
Oxidation of $H_2S$ in combustible gases to $SO_2$ as well as to $SO_3$ by $O_2$ or $O_3$ -containing gases.	Active catalysts are diluted by inert substances so that for 100 parts of the latter 1.5 parts of active catalyst are used; in case of a simultaneous discharge of the originating excess of reaction heat by streaming gases per 100 parts corresponding to 5 parts of the catalyst substance are used.	I.G. Farbenindustrie A.-G.: G.P. 634,427, Kl 26d, Aug. 28, 1936.
Oxidation of $H_2S$ with $O_2$ as well as air, also with $SO_2$ .	Active charcoal.	Krezil: <i>Chem.-Zig.</i> , 61, 247-249, 267-270 (1937).

Table 6. Catalytic Oxidation of Phosphorus and Its Compounds.

Reaction	Catalyst	Observer
Oxidation of P. $P_4 + 10H_2O \rightarrow 2P_2O_5 + 10H_2$ (industrial process).	$Fe_2O_3$ ; bauxite.	Phosphorus Hydrogen Co. (Liljenroth): G.P. 406,411 (1923). U.S.P. 1,594,372 (1923). G.P. 409,344 (1923).
	Cu and other metals or their compounds. Charcoal.	U.S.P. 1,605,960 (1923). G.P. 431,504 (1924).
Oxidation of red P by $H_2O$ at high temp. and pressure; 2 phases in the process: (1) oxidation of P; (2) oxidation of intermediate products; yield, 20-25% $H_3PO_4$ ; the partial pressure of $H_2$ in the range of 100-300 atm. does not markedly influence the reaction.	$NiO$ , $NiSO_4$ , or $Ni(NO_3)_2$ ; the presence of the catalyst accelerates only the dissolution of P; it does not influence the oxidation of the intermediate product.	Buschmakin, Ryssakow and Frost: <i>Zhur. Priklad. Khim.</i> , 6, 577-587 (1933).
Oxidation of yellow P by $H_2O$ at high temp. and under pressure; the yellow P is oxidized as readily as red P, the $H_3PO_4$ obtained containing less $H_3PO_3$ ; $H_2$ , however, contains more $PH_3$ and P vapor.	1% $NiO$ .	Buschmakin, Ryssakow and Frost: <i>Zhur. Priklad. Khim.</i> , 6, 588-606 (1933).
Oxidation of P with $H_2O$ at high temp. and pressures; T. 225°, $H_3PO_3$ formed exclusively; T. greater than 250°, $H_3PO_4$ formed; T. 225°, yield a mixture of $H_3PO_3$ and $H_3PO_4$ ; $H_3PO_3$ is in amount 9-10% of the total P; oxidation of the Na salt of $Na_2PO_3$ proceeds without further addition of alkali; only slow at temp. below 200°; above 250° on the contrary, it follows fast to $H_3PO_4$ .	$NaOH$ ; amount of alkali corresponding to that necessary for the preparation of $Na_3PO_4$ ; with $NaOH$ in amount sufficient to form mono-sodium salt; with so much alkali that $Na_3PO_4$ is formed from $H_3PO_4$ ; the oxidation proceeds fast even at 100° and completely to $Na_2HPO_4$ without formation of phosphine as side product; sufficient alkali addition causes absence of salt of sub-phosphoric acid as oxidation product.	Ipatieff and Usachev: <i>J. Am. Chem. Soc.</i> , 57, 300-302 (1935).
Oxidation of $PH_3$ by $H_2O$ under pressure to $H_3PO_4$ , $H_3PO_3$ and $H_2$ ; $H_3PO_3$ is oxidized by $H_2O$ to $H_3PO_4$ or decomposes into $PH_3$ and $H_2$ ; an excess of water prevents oxidation of $PH_3$ on the Ag surface; a lack of $H_2O$ causes a partial decomposition of $PH_3$ so that equilibrium is not attained.	Ag filings.	Buschmakin and Frost: <i>Zhur. Priklad. Khim.</i> , 6, 607-612 (1933).
Oxidation of $H_3PO_4$ ; $4H_3PO_4 \rightarrow 3H_2PO_4 + PH_3$ with increase in temp., the velocity of the following reaction increases: $PH_3 + 3H_2O \rightarrow H_3PO_3 + 3H_2$ ; T. 330°; heating up to 350° for 30 min. of a mixture of P and $H_3PO_4$ with definite amounts of $NH_3$ forms ammonium phosphate on cooling.	The search for a catalyst accelerating the oxidation reaction gave no positive results.	Buschmakin and Frost: <i>Ibid.</i> , 6, 613-620 (1933).

Table 6 (Continued).

Reaction	Catalyst	Observer
Oxidation of phosphorus vapors and $\text{PH}_3$ in blast furnace gases by $\text{O}_2$ ; the combustible gases, $\text{H}_2$ and $\text{CO}$ , are not burned thereby; during oxidation, N oxides are formed which are absorbed by alkali bases; the gas becomes poorer in N oxides than coking gas; thus this process is suitable especially for obtaining $\text{H}_2$ or for synthetic liquid fuels; the use of $\text{HNO}_3$ is very small and finally an acid is obtained representing a mixture of $\text{HNO}_3$ , $\text{HNO}_2$ , $\text{H}_2\text{PO}_4$ , $\text{H}_2\text{PO}_3$ and $\text{H}_2\text{PO}_2$ ; by heating this mixture to 90–92° the lower phosphoric acids change into ortho acids, from which pure $\text{H}_2\text{PO}_4$ is obtained.	50–55% $\text{HNO}_3$ .	Rosenkranz: <i>Izvest. Akad. Nauk. U.S.S.R.</i> , 75–99 (1938).

Table 7. Catalytic Oxidation of Various Inorganic Compounds.

Reaction	Catalyst	Observer
Oxidation of HCl by the Deacon process $2\text{HCl} + \frac{1}{2}\text{O}_2 \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$ .	$\text{CuCl}_2$ .	Deacon: E.P. 1,403 (1868). Rhenania Verein Chemische Fabriken: E.P. 229,334 (1925). Deacon: E.P. 505 (1873).
Oxidation of Mn salts by persulfate in aqueous $\text{H}_2\text{SO}_4$ : $2\text{Mn}^{++} + 5\text{S}_2\text{O}_8^{--} + 8\text{H}_2\text{O} \rightarrow 2\text{MnO}_4^{--} + 10\text{SO}_4^{--} + 16\text{H}^+$ ; the oxidation is independent of the conc. of $\text{MnSO}_4$ and proportional to the conc. of $\text{K}_2\text{S}_2\text{O}_8$ and $\text{Ag}_2\text{SO}_4$ ; two stages are postulated: (1) $\text{Ag}' + \text{S}_2\text{O}_8^{--} \rightarrow \text{Ag}^{++} + 2\text{SO}_4^{--}$ (proceeds slowly; measurable) (2) $5\text{Ag}^{++} + 2\text{Mn}^{++} + 8\text{H}_2\text{O} \rightarrow 5\text{Ag}' + 2\text{MnO}_4^{--} + 16\text{H}^+$ (instantaneous).	$\text{Ag}_2\text{SO}_4$ .	Benier and Kijowski: <i>Roczniki Chem.</i> , 14, 1004–1016 (1934); 15, 136–152 (1935).
Oxidation of $\text{Mn}^{++}$ to $\text{MnO}_4^{--}$ by $\text{Br}_2$ in an alkali solution and oxidation of $\text{Mn}^{++}$ to $\text{MnO}_4^{--}$ by $\text{Na}_2\text{S}_2\text{O}_8$ in an acid solution.	$\text{Ag}'$ , as well as $\text{Ca}^{++}$ (oxidation-reduction potentials of these ions are measured; addition of $\text{CuSO}_4$ increases the potential, while $\text{KNO}_3$ , $\text{NiSO}_4$ , $\text{AuCl}_3$ , $\text{ZnSO}_4$ decrease it).	Erisstawi: <i>Zhur. Obshchei Khim.</i> , 7 (69), 1713–1720 (1937).
Oxidation of $\text{Mn}^{++}$ only to $\text{MnO}_2^{++}$ .	$\text{Hg}'$ , $\text{Na}'$ , $\text{Ba}^{++}$ , $\text{Al}^{+++}$ , $\text{Fe}'$ , $\text{Fe}^{++}$ , $\text{Sr}^{++}$ , $\text{Zn}^{++}$ , $\text{Cr}^{++}$ and $\text{Ni}^{++}$ ions.	
Oxidation.	Various oxidation stages of Cr, W, V, Fe, U (Fe and U, especially in the light); Mo, Cu, Ag, Hg, Co, Ni, Pb, Mn, Ce, Ti, I, Na, etc.	Sabatier: "Catalysis in Organic Chemistry," pp. 69, 356, 413.
Oxidation of $\text{H}_2$ to $\text{H}_2\text{O}$ ; $\text{SO}_2$ to $\text{SO}_3$ ; $\text{NH}_3$ to $\text{NO}$ .	Metals Pt, Rh, Ir, Pd, Os, Au, Ag, also mixed catalysts, e.g., Fe-W oxides and Hopcalite.	Badische Anilin- und Soda Fabrik: G.P. 283,824 (1914). G.P. 284,815 (1914). Keller: <i>Z. angew. Chem.</i> , 29, 208 (1916).
Oxidation of sulfohydryl compounds by $\text{H}_2\text{O}_2$ .	Inorganic catalysts.	Ghosh and Kar: <i>J. Indian Chem. Soc.</i> , 14, 249–253 (1937).
Oxidation of $\text{K}_3\text{Fe}(\text{CN})_6$ by $\text{O}_2$ to $\text{K}_3\text{Fe}(\text{CN})_6$ .	Oxide powders, fuller's earth, bone charcoal; chromium oxide (free from chromate obtained by heating the initial compounds in $\text{O}_2$ -free $\text{H}_2$ ); the preparation decomposes readily and this influences the activity of the Cr catalyst; Cr hydroxide dried at 105°, slightly active; starting at 250°, the activity increases, reaching a maximum at 450°, then drops	Kutzelnigg and Wagner: <i>Monatsh.</i> , 67, 231–240 (1936). Kutzelnigg: <i>Monatsh.</i> , 67, 241–247 (1936).

Table 7 (Continued).

Reaction	Catalyst	Observer
	rapidly to zero; at 200° a second weak maximum; active (olive brown) preparations are amorphous (shown by x-ray); the stronger glow, inactive green preparation has the smallest activity; preparations obtained from Cr ammonium, Cr oxalate and Cr nitrate decrease in activity in this sequence.	
Oxidation of KI by H <sub>2</sub> O <sub>2</sub> .	Amorphous and crystalline oxyhydrates of Fe <sup>+++</sup> compared with catalytic activity of hydroxides; explained by the presence of active H <sub>2</sub> in the OH groups; sorption experiments with Fe orthohydroxide (1), γ-FeOOH (2) and goetite (3) compared in 0.001N KOH; the sorption values for (1) and (2) are equally large, while for (3), very small.	Krause and Ernst: <i>Ber.</i> , <b>70</b> , 443-446 (1937).
Oxidation processes.	Pure sugar charcoal, charcoal from sugar and urea; charcoal from sugar + FeCl <sub>3</sub> ; charcoal from sugar + FeCl <sub>3</sub> + urea; activation temp. 590-600°; carbon hydrosols activate; the catalytic action of carbon hydrosols is slight.	Keegel, Suruda and Schwab: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 2483-2486 (1938).
Reaction between H <sub>2</sub> O <sub>2</sub> and O <sub>2</sub> .		
Oxidation of iodides by persulfates, KI-K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ; reaction is not influenced by the <i>m</i> -compounds of the catalyst; it is shown that there is a far-reaching dependence of catalytic activity on the reaction medium.	<i>p</i> -Compounds of 3-phenylene diamines have the greatest influence; the catalytic activity of <i>p</i> -phenylenediamine increases by methylation of NH <sub>2</sub> groups, but it decreases again for the tertiary base; in case of <i>o</i> -phenyldiamine the tetra methylation leads to a decrease in catalytic activity; the agglomeration of amino- groups in the molecule of <i>p</i> -amidophenol increases the catalytic effect with simultaneous displacement of the activity maximum with respect to pH.	Afanasiew: <i>Acta Physicochim. U.R.S.S.</i> , <b>8</b> , 37-46 (1938). Afanasiew: <i>Zhur. Fiz. Khim.</i> , <b>11</b> , 231-36 (1938); <b>11</b> , 237-41 (1938).
Oxidation of iodides by persulfates: I <sup>-</sup> -S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> reaction.	Tetramethyl- <i>p</i> -phenylene diamine, <i>p</i> -phenylenediamine and benzidine (the activity of these organic catalysts is higher than that of Fe <sup>++</sup> and Cu <sup>2+</sup> ); the activity of the catalysts depends on the pH and the nature of the buffer mixture; neutral salts with polyvalent anions decrease the activity of catalysts; as active forms of organic catalysts are assumed the semi-and holoquinone form.	Afanasiew: <i>Acta Physicochim. U.R.S.S.</i> , <b>8</b> , 491-502 (1938). Afanasiew: <i>Zhur. Fiz. Khim.</i> , <b>11</b> , 367-74 (1938).

## PART X

## Catalytic Oxidation in Organic Chemistry

Table 1. Catalytic Oxidation of Carbon.

Reaction	Catalyst	Observer
Oxidation of C by NaCl.	A precipitate of NaCl on glass formed by evaporation of a NaCl solution or volatilization of NaCl in a flame.	Taylor: <i>J. Am. Chem. Soc.</i> , <b>52</b> , 3025, 3026 (1930).
Oxidation of a sooty film produced from CH <sub>2</sub> Cl <sub>2</sub> in O <sub>2</sub> at 600°; on coarse glass particles, combustion velocity of soot is a	NaCl (the activating influence of NaCl by the action of H <sub>2</sub> O vapor upon soot and in the case of combustion with O <sub>2</sub> is	Kassel: <i>J. Am. Chem. Soc.</i> , <b>58</b> , 1309, 1310 (1936).

Table 1 (Continued).

Reaction	Catalyst	Observer
few seconds; on smooth glass particles, velocity practically unaffected; soot particles must be so oriented that they lie parallel to the contact surface.	different: in the first case the salt is impregnated in the C surface, while by combustion the O <sub>2</sub> molecules of the soot layer must first penetrate before the salt reaches there).	
Oxidation of pure C by air; T. 200–450°; C heated alone in air cannot be strongly oxidized; C heated in air and in N <sub>2</sub> gives about an equal amount (small) of CO <sub>2</sub> ; mixtures of C with the chromite catalyst give greatly increased amount of CO <sub>2</sub> when heated in air; in N <sub>2</sub> when heated, a smaller amount of CO <sub>2</sub> is formed, partially from desorbed gas and partially from reduction of the chromite.	Cu or Zn chromite.	Day and Robey: <i>Ind. Eng. Chem.</i> , <b>28</b> , 564–567 (1936).
Oxidation of graphite with water vapor to CO (water gas process); water gas equilibrium on activated graphite established at 570°.	CuO (strong action); decreasing activity in sequence for the oxide series: Cr, Ni, Fe, U, Ti, Mn, Co, Al; alkali carbonates especially favorable; decrease in activity follows the sequence: K, Na, Rb, Cs, Li; alkali bicarbonates act stronger than additivity predicts; however, the pure K carbonate remains in the first place in activity; Co <sub>2</sub> O <sub>3</sub> —K <sub>2</sub> CO <sub>3</sub> mixture; most active, ThO <sub>2</sub> , Hg, Te and Th oxide; Li carbonate; mixture of Li and K carbonate and U oxide and K carbonate.	Kröger and Melhorn: <i>Brennstoff-Chem.</i> , <b>19</b> , 157–169, (1938).
Highest water vapor decomposed with Co <sub>3</sub> O <sub>4</sub> —K <sub>2</sub> CO <sub>3</sub> mixture; unsaturated hydrocarbons formed with additions of alkalis.		

Table 2. Catalytic Oxidation of Carbon Monoxide (Industrial Process).

Reaction	Catalyst	Observer
Oxidation of combustible gas mixtures.	Heated Pt wire.	Humphrey: (1817).
Oxidation of CO, H <sub>2</sub> or HCN (acid) by air.	Slightly heated Pt spiral (after causing oxidation, becomes incandescent).	Davy: <i>Phil. Mag.</i> , <b>97</b> , 45 (1817).
Oxidation of CO to CO <sub>2</sub> ; T. 350–450° CO + H <sub>2</sub> O → CO <sub>2</sub> + H <sub>2</sub>	Metal catalysts finely dispersed: Ni and Co.	Naumann and Pistor: <i>Ber.</i> , <b>18</b> , 2724 (1885). Hoitsema: <i>Z. physik. Chem.</i> , <b>25</b> , 686 (1898). Hembert and Henry: <i>Compt. rend.</i> , <b>101</b> , 797 (1885).
Oxidation of CO. CO + H <sub>2</sub> O → CO <sub>2</sub> + H <sub>2</sub>	Ni or Co. Ni, Fe, Mn. Metal chromates. Co <sub>2</sub> O <sub>3</sub> (Fe <sub>2</sub> O <sub>3</sub> ) + Al <sub>2</sub> O <sub>3</sub> + K <sub>2</sub> O.	Mond and Langer: <i>E.P.</i> 12,608 (1888). G.P. 51,572 (1889). Badische Anilin- und Soda Fabrik: <i>G.P.</i> 292,615 (1912). Dupont (Lazier): <i>E.P.</i> 272,555 (1927). Evans and Newton: <i>Ind. Eng. Chem.</i> , <b>18</b> , 513 (1926). Dominik: <i>Przemysl Chem.</i> , <b>11</b> , 557 (1926). Neumann and Köhler: <i>Z. Elektroch.</i> , <b>34</b> , 218 (1928).
Oxidation of CO (purification of gases). CO + ½ O <sub>2</sub> → CO <sub>2</sub>	Hopcalite: (1) 50% MnO <sub>2</sub> 30% CuO 15% Co <sub>2</sub> O <sub>3</sub> 5% Ag <sub>2</sub> O (2) 60% MnO <sub>2</sub> 40% CuO	Frazer and Scalione: <i>U.S.P.</i> 1,345,323 (1919). Lamb: <i>U.S.P.</i> 1,422,211 (1919). Lamb, Bray and Frazer: <i>J. Ind. Eng. Chem.</i> , <b>12</b> , 217 (1920). Lamb, Scalione and Edgar: <i>J. Am. Chem. Soc.</i> , <b>44</b> , 738 (1922). Bray and Almquist: <i>Ibid.</i> , <b>45</b> , 2305 (1923). Bray and Doss: <i>Ibid.</i> , <b>48</b> , 2060 (1926).
Oxidation of CO-containing gases by H <sub>2</sub> CrO <sub>4</sub> to H <sub>2</sub> CO <sub>3</sub> .	HgO.	Hofmann: <i>G.P.</i> 307,614 (1920).

Table 2 (Continued).

Reaction	Catalyst	Observer
Oxidation of CO. (1) $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ (2) $2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2$	$\text{V}_2\text{O}_5$ .	Scalione and Frazer: E.P. 166,285, Aug. 11, 1921.
Oxidation of CO.	$\text{MnO}_2$ .	Whitesell and Frazer: <i>J. Am. Chem. Soc.</i> , <b>45</b> , 2841 (1923).
Oxidation of CO to $\text{CO}_2$ .	$\text{MnO}_2$ ; Co and Ag oxides. Hopcalite: (1) 60% $\text{MnO}_2$ 40% $\text{CuO}$ (2) 50% $\text{MnO}_2$ 30% $\text{CuO}$ 15% $\text{Co}_3\text{O}_4$ 5% $\text{Ag}_2\text{O}$	Benton: <i>Ibid.</i> , <b>45</b> , 887,900 (1923).
Oxidation of CO.	Quartz glass.	Benton and Williams: <i>J. Phys. Chem.</i> , <b>30</b> , 1487-1496 (1926).
Oxidation of CO.	$\text{CuO}$ or $\text{MnO}_2$ .	Hoskins and Bray: <i>J. Am. Chem. Soc.</i> , <b>48</b> , 1457 (1926).
Oxidation of CO to $\text{CO}_2$ .	Co, Fe as $\text{Fe}_2\text{O}_3$ , Cr and mixtures.	Evans and Newton: <i>Ind. Eng. Chem.</i> , <b>18</b> , 513 (1926).
Oxidation of CO.	Carrier with Fe-containing substances not penetrable for the converted gas.	Fourneau and Kibas: <i>Bull. soc. chim.</i> , <b>4</b> (39), 1587-1589 (1926).
Oxidation of CO to $\text{CO}_2$ .	Colloidal solution of basic Fe salt and a volatile acid molded to briquettes without Cl or S cpds.	Dominik: <i>Przemysl Chem.</i> , <b>11</b> , 557-562 (1926). Polish P. 8,572, Sept. 25, 1928.
Oxidation of CO	$\text{MnO}_2$ or $\text{CuO}$ .	Draper: <i>J. Am. Chem. Soc.</i> , <b>150</b> , 2037-2633 (1928).
Oxidation of CO.	$\text{Co}_3\text{O}_4$ , $\text{MnO}_2$ .	Marok and Wedekind: <i>Z. anorg. allgem. Chem.</i> , <b>186</b> , 49-76 (1929).
Oxidation of CO to $\text{CO}_2$ .	Fe, Ni, Co, as well as their oxides or carbonates.	Kneutzel: <i>J. Am. Chem. Soc.</i> , <b>52</b> , 437 (1930); <b>52</b> , 445 (1930).
Oxidation of CO to $\text{CO}_2$ .	Pt black.	Taylor, Kistiakowsky and Perry: <i>J. Phys. Chem.</i> , <b>34</b> , 748-752 (1930).
Oxidation of CO.	$\text{MnO}_2 + \text{NiO}$ or $\text{MnO}_2 + \text{Ag}_2\text{O}$ ; $\text{AgMnO}_2 + \text{NiO}$ ; $\text{MnO}_2 + \text{CoO}$ ; $\text{Ag}_2\text{O} > \text{MnO}_2 > \text{Co}_3\text{O}_4 > \text{NiO} > \text{CuO}$ ; $\text{MnO}_2 + \text{CoO}$ , ratio: 3 : 1, 1 : 1, 1 : 1, 1 : 3.	Neumann, Kröger and Iwanowski: <i>Z. Elektroch.</i> , <b>37</b> , 121-128 (1931).
Oxidation of CO.	Manganites of heavy metals, alkaline-earth metals, rare earths, Cu and Co.	I. G. Farbenindustrie A.-G.: E.P. 355,308, Sept. 17, 1931. F.P. 704,119, May 13, 1931.
Oxidation of CO.	Hopcalite: (1) 50% $\text{MnO}_2$ 30% $\text{CuO}$ 15% $\text{Co}_3\text{O}_4$ 5% $\text{Ag}_2\text{O}$	Pieters: <i>Chem. Weekblad</i> , <b>28</b> , 250 (1931).
Oxidation of CO.	$\text{Ag}_2\text{O}$ , $\text{MnO}_2$ (room temp.).	Pieters: <i>Z. anal. Chem.</i> , <b>85</b> , 113-117 (1931).
Oxidation of CO.	$\text{MnO}_2 + \text{Ag}_2\text{O}$ , or $\text{MnO}_2 + \text{CuO}$ .	Frazer: <i>J. Phys. Chem.</i> , <b>35</b> , 605 (1931).
Oxidation of CO.	Water vapor.	Passauer: <i>Z. physik. Chem. (A)</i> , <b>161</b> , 299-304 (1932).
Oxidation of CO to $\text{CO}_2$ . $2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2$	$\text{TiO}_2$ , $\text{Co}_3\text{O}_4$ , or $\text{Fe}_2\text{O}_3$ .	Engelder and Miller: <i>J. Phys. Chem.</i> , <b>36</b> , 1345-1358 (1932).
Oxidation of CO.	Cupric chromate, Fe, Ni, Co chromite.	Lory: <i>Ibid.</i> , <b>37</b> , 685-692 (1933).
Oxidation of CO.	Adsorption cpds. such as $\text{MnO}_2$ .	Mathieu, Lévy and Geloso: <i>Bull. soc. chim. (4)</i> , <b>53</b> , 1039 (1933).
Oxidation of CO.	Alloy: 25% Mn+10% Pb+60% Cu, or 25% Mn+75% Cu, or 90% Fe+10% Cu	Barker: U.S.P. 1,916,249, July 4, 1933.

Table 2 (Continued).

Reaction	Catalyst	Observer
Oxidation of CO.	FeSO <sub>4</sub> or MnSO <sub>4</sub> replaced by NH <sub>3</sub> +chromic acid; CuSO <sub>4</sub> treated with Na <sub>2</sub> CO <sub>3</sub> +Cr <sub>2</sub> O <sub>3</sub> and HNO <sub>3</sub> .	Dupont (Larson): U.S.P. 1,908,484, May 9, 1933.
Oxidation of CO.	211.0 g. Co(NO <sub>2</sub> ) <sub>2</sub> · 6H <sub>2</sub> O + 34.5 g. NaOCl.	Frazer: U.S.P. 1,937,689, Dec. 5, 1933.
Oxidation of CO to CO <sub>2</sub> .	Mn <sup>IV</sup> (prepared from a mixture of the 2- and 4-valent Mn); Ni from NiCrO <sub>4</sub> ; Ni from 3NiO · Al <sub>2</sub> O <sub>3</sub> treated with NaOH	Intermetal Corporation (Jeunes): U.S.P. 1,937,489, Nov. 28, 1933.
Oxidation of CO; T. 160–250°.	Mixed crystals of 25% Fe <sub>2</sub> O <sub>3</sub> , 75% Al <sub>2</sub> O <sub>3</sub> , or 52.9 mol % Fe <sub>2</sub> O <sub>3</sub> , 47.10 mol % Al <sub>2</sub> O <sub>3</sub> .	Eckell: <i>Z. Elektroch.</i> , <b>39</b> , 807–815 (1933).
Oxidation of CO.	MnO <sub>2</sub> +CuO.	Mathieu and Lévy: <i>Compt. rend.</i> , <b>196</b> , 1319–1321 (1933).
Oxidation of CO.	MnO <sub>2</sub> (3 stages in activity of the catalyst; second stage, important).	Mathieu, Lévy and Geloso: <i>Bull. soc. chim.</i> (4), <b>53</b> , 1039–1050 (1933).
Oxidation of CO to CO <sub>2</sub> ; T. 500° CO+H <sub>2</sub> O → CO <sub>2</sub> +H <sub>2</sub> maximum in oxidation velocity; the catalyzed reaction is very sensitive toward small amounts of H <sub>2</sub> or water vapor; when their concentration increases, the reaction velocity increases rapidly and without limit; it is assumed that H atom chains appear in the system which increase the total oxidation velocity.	NO <sub>2</sub> (gives off O <sub>2</sub> atoms); Fe glowing at 700°; CO, high activity, but not very stable; Co+MgO (resistance increased, but activity lowered); FeCO <sub>3</sub> (siderite) with 0.7% K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (highly active and stable).	Christ and Koehling: <i>Science</i> , <b>80</b> , 338 (1934).
Oxidation of CO.	MnO <sub>2</sub> (60%)+CuO <sub>2</sub> (40%), most active.	Roginsky and Zeldowitsch: <i>Acta Physicochim. U.R.S.S.</i> , <b>1</b> , 554–594, 595–610 (1936).
Oxidation of CO.	MnO <sub>2</sub> (finely dispersed); CO, O <sub>2</sub> and CO <sub>2</sub> are all adsorbed on MnO <sub>2</sub> ; adsorption of CO and O <sub>2</sub> marked only below 0°; activated adsorption of CO accompanied by oxidation to CO <sub>2</sub> ; MnO <sub>2</sub> +CO → MnO+CO <sub>2</sub> +41,000 cal.	Zeldowitsch: <i>Ibid.</i> , <b>1</b> , 449–464 (1934). Zeldowitsch: <i>Zhur. Fiz. Khim.</i> , <b>6</b> , 234–242 (1935).
Oxidation of CO; T. 80°; O <sub>2</sub> present in excess so that PtO <sub>2</sub> is not self-reduced; with O <sub>2</sub> in excess, oxidation in the presence of Pt starts at 184° and is complete at 218°; with CO in excess the reaction starts only at 218°.	PtO <sub>2</sub> ; Pt black obtained by reduction of PtO <sub>2</sub> by CO is an extremely fine dispersion which influences the oxidation of CO catalytically; small amounts of Fe in PtO <sub>2</sub> accelerates its reduction.	McKinney: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 2577 to 2580 (1934).
Oxidation of CO.	Quartz (water, negative catalyst).	Bradford: <i>J. Chem. Soc.</i> , 73–75 (1934).
Oxidation of CO.	Oxides of Ni and Cu.	Bone: <i>Proc. Roy. Soc. London (A)</i> , <b>112</b> , 474–99 (1926); (Refer to C. 1927 I 245).
Oxidation of CO.	Argon with 40% ionization.	Rosenblum: <i>J. Phys. Chem.</i> , <b>38</b> , 683–688 (1934).
Oxidation of CO.	FeCO <sub>3</sub> +0.7% K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> on MgO (which renders it more stable) glowing at 700°.	Iwanowski, Braude and Panina: <i>Zhur. Khim. Prom.</i> , <b>2</b> , 37–44 (1934).
Oxidation of CO.	First stage oxidation: Cr <sub>2</sub> O <sub>3</sub> containing Fe + active charcoal; second stage hydrogenation: Ni+ThO <sub>2</sub> +active charcoal.	Kemmer: G.P. 617,565, Kl 26a, Aug. 21., 1935.
Oxidation of CO.	Rh alloy or perhenates.	Platonow, Anissimow and Krascheninnikowa: <i>Ber.</i> , <b>68</b> , 761–765 (1935).

Table 2 (Continued).

Reaction	Catalyst	Observer
Oxidation of CO.	Fe(OH) <sub>3</sub> mixed with Na <sub>2</sub> CO <sub>3</sub> and the mixture solidified by a dehydrating binding agent—cement.	Non-Poisonous Gas Holding Co., Ltd.: F.P. 777,546, Feb. 22, 1935.
Oxidation of CO with water vapor; T. 410–600°; space velocities 342 and 3,920.	Fe-Al oxide and cast iron both activated with K <sub>2</sub> CO <sub>3</sub> .	Simek and Rassler: <i>Commun. Kohlenforsch. Inst. Prague</i> , 2, 125–141 (1935).
Oxidation of CO; T. 1250° heated electrically (in CO-air mixture, heating velocity essentially greater than in pure CO); the velocity of catalytic combustion of CO over the catalyst increases with temp., decreasing with further increase and is zero at about 1200°.	Pt and Pd wire, 0.001 in. in diameter; no explosion takes place at low temp., CO is bound to active places of Pt; at 400° O <sub>2</sub> passes on to the place of CO; at 1200° it is desorbed and catalysis disappears; further increase in temp. causes CO sorption, but on a second kind of active places; while in the case of CO-O, lies the region of complete desorption; in experiments with H <sub>2</sub> , a decrease in catalytic activity observed.	
Oxidation of CO to CO <sub>2</sub> . CO + H <sub>2</sub> O → CO <sub>2</sub> + H <sub>2</sub> .	Fe(OH) <sub>3</sub> mixed with Na <sub>2</sub> CO <sub>3</sub> and the mixture solidified by means of dehydrating agents, e.g., cement; the initial substances are ground before and during the preparation of the mass and moistened after addition of cement; preparation of the catalyst follows in a rotating drum.	Non-Poisonous Gas Holding Co., Ltd.: F.P. 777,546, Feb. 22, 1935.
Oxidation of CO; the existence of a critical low pressure limit, 0.522 mm., is found for (1) the reaction of CO with O <sub>2</sub> in gas and (2) the oxidation of CO by oxygen of the catalyst; high pressure oxidation takes place directly due to the presence of O <sub>2</sub> in the gas phase.	MnO <sub>2</sub> .	Charachorin, Elowitz and Roginsky: <i>Acta Physicochim. U.R.S.S.</i> , 3, 503–508 (1935). Charachorin and Elowitz: <i>Ibid.</i> , 5, 325–354 (1936). Elowitz and Roginsky: <i>Ibid.</i> , 7, 295–310 (1937).
Oxidation of CO with water vapor (best method for depoisoning gas).	MnO <sub>2</sub> .	Wysocki and Eskreis: <i>Gas i Woda</i> , 16, 389–393 (1936).
Oxidation of CO; T. 500–600°.	Cu chromite (CuO, Cr <sub>2</sub> O <sub>3</sub> or Cu(CrO <sub>2</sub> ) <sub>2</sub> ) (prepared by conversion of Cu(OH) <sub>2</sub> with CrO <sub>3</sub> to form Cu(CrO <sub>4</sub> ) <sub>2</sub> ; Cu(OH) <sub>2</sub> is produced from Cu(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O by precipitating with NH <sub>3</sub> ).	Frazer: U.S.P. 2,031,475, Feb. 18, 1936.
Oxidation of CO to CO <sub>2</sub> in the presence of H <sub>2</sub> ; 50.0–95.0% H <sub>2</sub> , 0.5–2.0% CO, remaining % CO <sub>2</sub> .	Pressed grains from powdered Cu and finely divided Mn oxides (having less than 1 and more than ½ atom of active O <sub>2</sub> per atom Mn and obtained from MnO <sub>2</sub> by reduction with gases at temp. of 100–175°).	Intermetal Corporation (Jeunes): U.S.P. 2,103,221, Dec. 21, 1937.
Oxidation of CO to CO <sub>2</sub> . 1% CO 1% O <sub>2</sub> 74% H <sub>2</sub> 24% CO <sub>2</sub>	A mixture of Mn oxides consisting principally of Mn <sub>2</sub> O <sub>3</sub> ; the remaining MnO <sub>2</sub> is reduced below 150° to produce a mixture which has less than 1 but more than ½ atom of active oxygen per atom Mn.	Jeunes: U.S.P. 2,103,219 and 2,103,220, Dec. 22, 1937.
Oxidation of CO to CO <sub>2</sub> with water vapor.		van Dijk: <i>Gas (Gravenhage)</i> , 57, 225–229 (1937).
Oxidation of CO to CO <sub>2</sub> ; 2CO + O <sub>2</sub> → 2CO <sub>2</sub> (the surface conc. of O <sub>2</sub> was determined by electrical conductivity measurements); the excess O <sub>2</sub> content and the surface conc. of O <sub>2</sub> is smaller than in the presence of O <sub>2</sub> alone (with-	NiO.	Wagner and Hauffe: <i>Z. Electroch.</i> , 44, 172–178 (1938).

Table 2 (Continued)

Reaction	Catalyst	Observer
out a catalyst) with equal partial pressure; the reaction of CO with O <sub>2</sub> from the catalyst phase determines the time factor, the completion of the used O <sub>2</sub> from the gas phase follows quickly.		
Oxidation of combustible gases.	(CuO) <sub>2</sub> —Cr <sub>2</sub> O <sub>3</sub> intimately mixed with a reducible Ag salt such as AgNO <sub>3</sub> solution, whereby small amounts of free Ag are finely dispersed on heating.	Frazer: U.S.P. 2,092,059, Sept. 7, 1937.
Oxidation of CO.	Mo steels with considerable content of Mn (5%).	
Oxidation of CO.	Dehydrated Hopcalite has a higher activity than Hopcalite containing a considerable amount of bound water (prepared according to Whitzel and Frazer method); water is removed at 180° with simultaneous degasing; the dependence of the amount of CO oxidized by the O <sub>2</sub> of the Hopcalite surface on its activity is linear.	Bruns: <i>Acta Physicochim.</i> U.R.S.S., 7, 875-882 (1937).
Oxidation of CO; as mechanism for this reaction on Fe <sub>2</sub> O <sub>3</sub> is proposed one in which members of the reaction chain consist of oxycarbonyl compounds of the type (Fe <sub>2</sub> O <sub>3</sub> )(CO), formed as intermediate phase; reaction over Fe <sub>2</sub> O <sub>3</sub> powder is of the first order; reaction over Fe <sub>2</sub> O <sub>3</sub> obtained from the aerosol is of a zero order.	Fe <sub>2</sub> O <sub>3</sub> (precipitated and powdered from an aerosol); activation energy is the same for both catalysts: 8150 Cal.; the adsorption of CO is an activated adsorption with activation energy for the powder = 4450 Cal. and for the aerosol = 2040 Cal.	Iwanow and Kobosew: <i>Zhur. Fiz. Khim.</i> , 10, 1-17 (1937).
Oxidation of CO to CO <sub>2</sub> T. 300-400°.	Activity of CuO powder and precipitated CuO aerosol compared, the latter obtained by electrical dispersion and precipitation in an electrostatic field; the relative activity of the aerosol increases with temp., whereby at 250° the aerosol is 765 times more active than the corresponding powder; energetic catalysis in case of aerosols lies at temp. 200° lower than in the case of CuO powder; x-rays show the same structure for both catalysts; however, a smaller crystallite size in case of the Cu aerosol; a further decrease of the same obtained after catalysis.	Bessalow and Kobosew: <i>Zhur. Fiz. Khim.</i> , 9, 815-827 (1937).
Oxidation of CO	Mixture of SiO <sub>2</sub> -containing material, e.g., powdered glass, plaster of paris and the catalytic substance CuSO <sub>4</sub> .	Finn and Frohwitter: U.S.P. 2,106,910, Feb. 1, 1938.
Oxidation of CO to CO <sub>2</sub> ; CO + H <sub>2</sub> O → CO <sub>2</sub> + H <sub>2</sub> .	Cu and CoO are placed under very high pressure and heated to 500-1100°; after cooling, they are broken and converted into grains of desired size.	General Electric Co. (Ferguson): U.S.P. 2,106,597, Jan. 25, 1938.
Oxidation of CO: 2CO + O <sub>2</sub> = 2CO <sub>2</sub> ; the discontinuous change of the catalyst action coincides with the starting loss in ferromagnetism; the gradual loss of ferromagnetism starts at 272°.	MgO · Fe <sub>2</sub> O <sub>3</sub> , crude iron, special steel at temp. at which changes in the ferromagnetism of the catalyst substance take place; (1) MgO · Fe <sub>2</sub> O <sub>3</sub> (obtained by precipitating a mixture of equivalent amounts of MgCl <sub>2</sub> and FeCl <sub>3</sub> solution with NaOH), washing and glowing at 700°; (2) crude iron of the composition: 93.098% Fe, 4.26% C, 0.98% Si, 0.023% P, 0.029% S, 1.61% Mn.	Hedvall and Berg: <i>Z. physik. Chem. (B)</i> , 41, 388-395 (1938)
Curie-Interval: 710-737°.		



Table 2 (Continued).

Reaction	Catalyst	Observer
<p><i>J</i> Oxidation of CO with water vapor; the activation energy for the water gas reaction is calculated as 25,000 cal.; temp. coefficient determined to be 1.23; equations are deduced which permit calculation of mass transport and catalytic activity for the reaction, expressed in absolute mass units, so that determination of required amount of catalyst is made possible; from these equations it is found that the velocity coefficient (<math>K</math>) for heterogeneous reaction increases with rising temp.; for the water gas reaction the temp. dependence is expressed as: <math>\log K = 5640/T_m = 11.71</math>, where <math>T_m</math> is the average temp. of the interval investigated.</p>		Laupichler: <i>Ind. Eng. Chem.</i> , <b>30</b> , 578-586 (1938).
Oxidation of CO by $H_2O$ into $CO_2$ and $H_2$ .	$CoCO_3$ to which 5-25% $CoO$ has been added is heated for 3 min. to 900-1100°, and likewise, after treatment with oxidizing gases, is reduced.	Storch: U.S.P. 2,118,829, May 31, 1938.
Oxidation of CO: a definite activation stage through molecular oxygen is assumed for all oxidation reactions; the active form is a definite oxygen form, and in the case of metal catalysts serves the activated adsorbed $O_2$ as active surface oxygen, while for the oxide catalysts, the excess $O_2$ dissolved in the surface layer (in the interstices of the lattice space) performs the task.	$MnO_2$ .	Roginsky: <i>Acta Physicochim. U.R.S.S.</i> , <b>9</b> , 475-500 (1938).
Oxidation of CO; T. 320-400° 6-20 atmospheres pressure.	A catalyst consisting of calcined $MgCO_3$ , $CaCO_3$ and charcoal is ground together with an asphalt emulsion and heated at 600-800° in the absence of air.	American Magnesium Metals Corporation (Hausging): G.P. 677,103, Kl 12i, June 19, 1939.
<p>Oxidation of CO:  <math>2CO + O_2 \rightarrow 2CO_2</math>            T. 20° and 100°; the <math>CO_2</math> conc. scarcely acts upon the reaction velocity; at low pressures a chemisorption of CO takes place on the catalyst, which is very much favored by the adsorption of water; at <math>5 \cdot 10^{-3}</math> to <math>1.0 \cdot 10^{-1}</math> mm. Hg pressure the reaction velocity is almost independent of the <math>O_2</math> conc. and is proportional to the conc. of CO; by a chemisorption of 2% and more, it follows the equation:  <math>dq/dT = ae^{-ae}</math>            where <math>q</math> = CO conc. by a smaller chemisorption (<math>\sim 1\%</math>), the reaction proceeds according to the first order.</p>	<p><math>MnO_2</math>; the surface of <math>MnO_2</math> does not become uniform by drying up to 180°; as intermediate steps are assumed:  <math>MnO_2 + CO \rightleftharpoons MnO_2 \cdot CO</math>  <math>MnO_2 \cdot CO + O_2 \rightarrow MnO_2 \cdot O + CO_2</math>  <math>MnO_2 \cdot O + CO \rightarrow MnO_2 + CO_2</math>            the step  <math>MnO_2 \cdot CO \rightarrow MnO + CO_2</math>            is not feasible.</p>	Jelowitsch and Korndorf: <i>Zhur. Obshchei Khim.</i> , <b>9</b> , 673-681, 714-727 (1939).

Table 3. Catalytic Oxidation of Methane (Industrial Process).

Reaction	Catalyst	Observer
Oxidation of $CH_4$ to $H_2$ .	Bricks.	Vail: (1868). Vail: "Der Wasserstoff," p. 52, Braunschweig, 1925.
Oxidation of $CH_4$ to $H_2$ . $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	Lime.	Tessé du Motay: U.S.P. 229,338 (1879).
Oxidation of $CH_4$ to $H_2$ ; T. 350-450°.	Ni or Co on fireproof material.	Mond and Langer: G.P. 51,572 (1889).

Table 3 (Continued).

Reaction	Catalyst	Observer
Oxidation of $\text{CH}_4$ to $\text{H}_2$ ; T. 1100-1200°.	Fe, also coke.	Bunte and Mayer: <i>J. Gasbel-leucht.</i> , 37, 84 (1894).
Oxidation of $\text{CH}_4$ with $\text{O}_2$ to $\text{HCHO}$ . $\text{CH}_4 + \text{O}_2 \rightarrow \text{HCHO} + \text{H}_2\text{O}$	Cu on a carrier.	Bone and Wheeler: <i>J. Chem. Soc.</i> , 83, 1074 (1903). Sabatier and Maïhle: <i>Compt. rend.</i> , 142, 1394 (1906). Glock: G.P. 109,104
Oxidation of $\text{CH}_4$ to $\text{H}_2$ . $2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 2\text{H}_2$	Pt, Pd, Ag, Cu.	Bone and Andrew: <i>Proc. Chem. Soc.</i> , 22, 78 (1906).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ .	Ni, Co on ton pieces.	Naus: G.P. 226,609 (1909).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ .	Wire gauze of Ni, Co, or Pt.	Dieffenbach and Moldenhauer: G.P. 229,406 (1909). Hofmann: G.P. 469,432, Kl 12, Dec. 20, 1928.
Oxidation of $\text{CH}_4$ to $\text{H}_2$ . $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	Ni (NiO) on MgO.	Badische Anilin- und Soda Fabrik: G.P. 296,866 (1912).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ . $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	Fe-Cr alloy.	Nitrogen Corporation (Clancy): U.S.P. 1,425,579, Aug. 15, 1922.
Oxidation of $\text{CH}_4$ with $\text{CO}_2$ to $\text{H}_2$ ; T. 900 and 1100°. $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ excess $\text{CO}_2$ ; practically quantitative conversion.	Ni or NiO.	Badische Anilin- und Soda Fabrik: G.P. 306,301 (1920).
Oxidation of $\text{CH}_4$ with $\text{O}_2$ to $\text{H}_2$ ; T. 1200-1300°. $2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 2\text{H}_2$	Pt, Pd, Ag, or Cu; Fe, Co, Ni, or their oxides; oxides of V; Ni especially good contact.	Badische Anilin- und Soda Fabrik: G.P. 403,049 (1922).
Oxidation of $\text{CH}_4$ with $\text{CO}_2$ in the isoprene lamp or using metal catalysts to $\text{HCHO}$ .	Cu, Ag, Ni, or Al filings.	Plausson and Vielle: G.P. 367,343 (1923). E.P. 156,148 (1920). F.P. 532,561 (1922).
<i>J</i> Oxidation of $\text{CH}_4$ with $\text{O}_2$ to $\text{HCHO}$ ; T. 200°.	Boric acid on clay.	Badische Anilin- und Soda Fabrik: G.P. 397,213 (1924). Bibb: U.S.P. 1,392,886 (1921).
Oxidation of $\text{CH}_4$ with water vapor to $\text{H}_2$ .	Coked coal with metallic or metal oxide additions.	Cumberland Coal and Power, Ltd.: E.P. 181,062 (1922).
Oxidation of $\text{CH}_4$ to $\text{HCHO}$ ; 5.8% $\text{CH}_4$ and 94.2% air gives a 40% yield $\text{HCHO}$ .	Mixture of oxides: Cu, Fe, Mn, Cr, e.g., $\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ .	Kaiser: F.P. 588,099 (1925).
Oxidation of $\text{CH}_4$ to $\text{HCHO}$ .	Mixture of oxides: Cu, Fe, Mn, Cr, e.g., $\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ using pumice, asbestos or quartz as carriers.	Bakelite Co. G.P. 411,215 (1925).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ . $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$	Ni + $\text{CeO}_2$ ( $\text{ThO}_2$ ).	I'Azote, Inc.: U.S.P. 1,713,325 (1927).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ .	Fe, Co, or Ni. Fe-Cr alloy.	Urbain: F.P. 641,195 (1927).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ .	Fe (Co, Ni) + difficultly reducible oxides.	Urbain: E.P. 267,535 (1927).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ .	Fe (Co, Ni) + Cr (V, alkali).	Urbain: E.P. 288,662 (1926).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ . $2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 2\text{H}_2$	$\text{MnO}_2$ , NiO and $\text{Co}_2\text{O}_3$ .	Jaut and Hawk: <i>J. Am. Chem. Soc.</i> , 49, 1459-1460 (1927).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ . $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	Fe (Co, Ni) + difficultly reducible oxides.	I. G. Farbenindustrie A.-G.: E.P. 267,535 (1927). E.P. 288,662 (1927).
Oxidation of $\text{CH}_4$ to $\text{H}_2\text{O}$ . $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	CuO with metalized silicic acid gel; Pt plated silicic acid gel.	Reyerson and Sweeringen: <i>J. Phys. Chem.</i> , 32, 192 (1928). Kobe and Brookben: <i>Ind. Eng. Chem., Anal. Ed.</i> , 6, 35 (1934).

Table 3 (Continued).

Reaction	Catalyst	Observer
Oxidation of $\text{CH}_4$ with $\text{CO}_2$ to $\text{H}_2$ ; T. 900–1000°. $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$	Ni or Cu + $\text{Al}_2\text{O}_3$ .	Fischer and Tropsch: <i>Brennstoff-chem.</i> , <b>9</b> , 39 (1928).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ . (1) $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ (2) $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$ T. 1300°, quantitative conversion; temp. decreased by mixed catalysts.	Ni + $\text{Al}_2\text{O}_3$ ; Co + $\text{Al}_2\text{O}_3$ .	Kubota and Jamanake: <i>Sci. Papers Inst. Phys. Chem. Research (Tokyo)</i> , <b>14</b> , 26 (1930). Fischer and Tropsch: <i>Brennstoff-chem.</i> , <b>9</b> , 39 (1928).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ . $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$	100 Ni atoms/1 g. molecule of added oxides.	Kubota and Jamanake: <i>Bull. Chem. Soc. Japan</i> , <b>4</b> , 211–220 (1929).
Oxidation of $\text{CH}_4$ . $2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 2\text{H}_2$	V oxide.	Campbell: <i>J. Soc. Chem. Ind.</i> , <b>48T</b> , 93 (1929).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ . $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$	Ni + $\text{Al}_2\text{O}_3$ ( $\text{ZrO}_2$ , $\text{ThO}_2$ , $\text{CaO}$ , $\text{CdO}$ , $\text{ZnO}$ ); 1 g. mol $\text{MgO}$ + 1 g. atom Ni.	Kubota and Jamanake: <i>Sci. Papers Inst. Phys. Chem. Research (Tokyo)</i> , <b>11</b> , 28–34 (1930).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ using water vapor, $\text{O}_2$ , or $\text{CO}_2$ .	Mixture of Fe, Ni or Co with compounds of Al containing O, Si, C. B. P. e.g., kaolin or bauxite	I. G. Farbenindustrie A.-G.: E.P. 323,855 (1930). F.P. 677,826 (1930).
Oxidation of $\text{CH}_4$ with water vapor to $\text{H}_2$ and $\text{CO}$ ; T. greater than 700°; to get rid of CO the mixture of gases is passed over the same catalyst at 400–500° and the CO oxidized with water vapor to $\text{CO}_2$ (industrial process).	Mixture of charcoal with Fe or Ni (700°).	Klukwin: "Conversion of Methane." Moschimenergostry. Leningrad, 1940.
Oxidation of $\text{CH}_4$ in a mixture consisting of 20% $\text{CH}_4$ and 80% $\text{H}_2$ led through an electric arc, the $\text{C}_2\text{H}_2$ formed being removed by active charcoal and treated with water vapor at 1100°; yield, 84.8% $\text{H}_2$ .	Ni on $\text{Al}_2\text{O}_3$ . Ni or NiO-alumina contact; long contact chambers made of Cr-Ni steel; T. below 1000°.	I.G. Farbenindustrie A.-G.: (Wietzel, Starke and Eisenhut): G.P. 488,502 (1930). G.P. 558,430 (1932). G.P. 570,026 (1933).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ . (1) T. 850–900°, and (2) T. 1000°. $2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2$	A weak acid solution of Ce, Cd + Al nitrate.	I. G. Farbenindustrie A.-G.: U.S.P. 1,813,478, July 7, 1931.
Oxidation of $\text{CH}_4$ to $\text{H}_2$ . (1) T. 850–900°, and (2) T. 1000°. $2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2$	(1) Silica gel with Ni or Co; (2) Ni + $\text{Al}_2\text{O}_3$ .	Joshikawa: <i>Bull. Inst. Phys. Chem. Research (Tokyo)</i> , <b>10</b> , 45 (1931).
Oxidation of $\text{CH}_4$ with water vapor to $\text{H}_2$ .	Fe, Co, Ni catalysts on artificial Al silicate or unburned Al compounds, such as bauxite or kaolin.	I. G. Farbenindustrie A.-G.: (Wietzel and Hennicke): F.P. 710,626 (1931). G.P. 554,551 (1931). G.P. 565,387 (1931). E.P. 323,855 (1930).
Oxidation of $\text{CH}_4$ with a mixture of air and water vapor to $\text{H}_2$ .	Melted $\text{Al}_2\text{O}_3$ .	Hydro-Nitro, S.A.: F.P. 723,817 (1932).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ .	Cu, $\text{V}_2\text{O}_5$ , $\text{CeO}_2$ .	Faith, Swan, Jr. and Keyes: <i>Ind. Eng. Chem.</i> , <b>25</b> , 224 (1933).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ ; T. 850–950°. $2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 2\text{H}_2$	Fireproof porous material impregnated with $\text{Ni}(\text{NO}_3)_2$ .	Padovani and Franchetti: <i>Giorn. chim. ind. applicata</i> , <b>15</b> , 429–432 (1933).
Oxidation of $\text{CH}_4$ -containing outlet gases from coal hydrogenation to $\text{H}_2$ ; T. 650°; yield, 90% $\text{H}_2$ .	Ni catalyst activated by $\text{Al}_2\text{O}_3$ containing 0.01–0.02 g. mol $\text{K}_2\text{CO}_3$ g. atom Ni.	Takenaka: <i>J. Fuel Soc. Japan</i> , <b>12</b> , 57 (1933).
Oxidation of $\text{CH}_4$ with excess of water vapor to $\text{H}_2$ ; T. 550°; high pressure.	Ni or Co oxide + $\text{Al}_2\text{O}_3$ ; equal parts $\text{Ni}(\text{OH})_2$ , $\text{Al}(\text{OH})_3$ and $\text{MgO}$ with $\text{NiNO}_3$ solution containing 1% $\text{KOH}$ ; dried at 115–135°.	Standard Oil Development Co. (Young, Hauks and Freyermuth): U.S.P. 1,904,592 (1933). U.S.P. 1,904,593 (1933). Standard Oil Development Co. (Shepard): U.S.P. 1,998,401 (1935).

Table 3 (Continued).

Reaction	Catalyst	Observer
Oxidation of $\text{CH}_4$ to $\text{H}_2$ .	Cu-Fe oxide: 500° Cu-Ce oxide: 550° Cu-Cr oxide: >600° Cu-U oxide Cu-U oxide } 700° Cu-Mo oxide Addition of Fe oxide assures complete oxidation of $\text{CH}_4$ by $\text{CuO}$ .	Arnell: <i>J. Soc. Chem. Ind.</i> , <b>53</b> , 89-92 (1934).
Oxidation of coke gas containing $\text{CH}_4$ .	A mixture composed of: 11.75% Ni 1.75% $\text{Cr}_2\text{O}_3$ 3.00% $\text{Al}_2\text{O}_3$ and kaolin.	Finkelstein and Sabolotzki: <i>Ukrain. Khim. Zhur.</i> <b>9</b> , 263 (1934).
Oxidation of $\text{CH}_4$ or methane-containing gases with water vapor to $\text{H}_2$ ; T. 600°.	Highly active charcoal with added metals or metal cpds. such as carbonates, oxides, hydroxides, or carbonyls.	Harter: G.P. 602,111 (1934).
Oxidation of $\text{CH}_4$ with water vapor to $\text{H}_2$ .	Ni- $\text{Al}_2\text{O}_3$ (specially prepared).	I. G. Farbenindustrie A.-G. (Stöweker): G.P. 617,593, Kl 12g Gr 14, July 28, 1925.
Oxidation of $\text{CH}_4$ with air: 1-5% $\text{CH}_4$ , 760-970° 20-70% $\text{CH}_4$ , temp. decreases 70% $\text{CH}_4$ , 380° 1-4% $\text{CH}_4$ , 900-1200° 2% $\text{CH}_4$ } 200° 1-2% $\text{H}_2$ } 1% $\text{CH}_4$ , 900°	Pt wire (a monomolecular oxygen layer at 800°); the adsorbed $\text{O}_2$ passes into the gas phase and then starts the oxidation of $\text{CH}_4$ .	Davies: <i>Phil. Mag. (A)</i> , <b>21</b> , 513-531 (1936).
Oxidation of $\text{CH}_4$ with $\text{O}_2$ to $\text{H}_2$ ; T. 700-850°; at this temp. the induction period is practically independent of the length of the Pt contact or its surface; however, the induction period is found to be greater with the catalyst than without it.	Pt wire, 1.5-20.0 cm. long and 0.2 mm. in diameter.	Poljakow and Grianenko: <i>Acta Physicochim. U.R.S.S.</i> , <b>6</b> , 587-608 (1937).
Oxidation of $\text{CH}_4$ to $\text{H}_2$ .	Sn, Fe, Al phosphates + 0.13% $\text{HCl}$	
Oxidation of $\text{CH}_4$ to $\text{H}_2$ . $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	Fe (Co or Ni) + Cr (V) oxides.	
Oxidation of methane; the kinetics of the reaction agree with a chain mechanism; investigation of the dependence of the branching of the chain upon the magnitude of the surface of the solid phase is assumed to indicate that heterogeneous-homogeneous catalysis is involved.	Solid phase.	Poljakow and Kornejewa: <i>Acta Physicochim. U.R.S.S.</i> , <b>6</b> , 755-768 (1937); <i>Zhur. Fiz. Khim.</i> , <b>9</b> , 260-268 (1937).

Table 4. Catalytic Oxidation of Paraffins.

Reaction	Catalyst	Observer
Oxidation of paraffins in liquid phase.	Cu salts ( $\text{CuSO}_4$ ), pumice, alkali metals, etc.	Schaal: G.P. 32,705 (1884). Bayer: G.P. 346,520 (1917).
Oxidation of paraffins in gaseous phase.	Cu.	Glock: G.P. 109,014 (1898).
Oxidation of paraffins in gaseous phase.	$\text{V}_2\text{O}_5$ .	Byrnesz: U.S.P. 1,675,029 (1916).
✓ Oxidation of paraffins in liquid phase.	Mn resinsates.	Flammer and Kelber: G.P. 406,866 (1919).
✓ Oxidation of paraffinic hydrocarbons to primary peroxides and fatty acids; T. 170°; 20 atm. $\text{O}_2$ pressure.	$\text{Na}_2\text{CO}_3$ .	Fischer and co-workers: <i>Ges. Abhandl. Kenntnis Kohle</i> , <b>4</b> , 48 (1919).
✓ Oxidation of paraffins in liquid phase.	$\text{NiO} + \text{CuO} + \text{Mn salts}$ .	Deutsche Erdölgesellschaft: B.P. 148,892 (1920).

Table 4 (Continued).

Reaction	Catalyst	Observer
Oxidation of paraffins with air or $O_2$ ; T. 100–110°.	1% Mn stearate; Os, Pt, Mn compounds.	Kelber: <i>Ber.</i> , <b>53</b> , 66 (1920). Ubbelohde and Eisenstein: <i>Mitt. deut. Forsch. Inst. Textilind. Dresden</i> , <b>H4</b> , (1918).
Oxidation of paraffins in gaseous phase.	$Cu + V_2O_5$ ; phosphates or borates.	Ellis-Foster: U.S.P. 1,697,263 (1921). Badische Anilin- und Soda Fabrik: G.P. 397,212 (1921). U.S.P. 1,487,020 (1921).
Oxidation of paraffinic hydrocarbons to fatty acids; paraffins oxidized by air blown through for many days; T. 115–125°; yield 66% higher fatty acids.	$HgO$ .	Ando: <i>J. Soc. Chem. Ind. (Japan)</i> , <b>24</b> , 7 (1921). Gault and Boisselet: <i>Mat. grasses</i> , <b>161</b> , 5930 (1921); <b>164</b> , 5998 (1924); <b>165</b> , 6105 (1922). Firma Pardubitzer Fabrik A.-G.: Swiss P. 82,057 P.P. 505,126
Oxidation of paraffins in gaseous phase.	Phosphate or borate.	Badische Anilin- und Soda Fabrik: G.P. 397,212 (1921). U.S.P. 1,487,020 (1921). E.P. 199,886 (1922).
Oxidation of paraffinic hydrocarbons to fatty acids.	2% Na, K, or Al.	Friedrich Bayer & Co.: G.P. 346,520 (1922).
Oxidation of paraffins.	Ni and Cu salts.	Deutsche Erdölgesellschaft: P.P. 520,106 (1921).
Oxidation of paraffins.	Hetero-complexes of Mo, W, U and Co oxides.	James: <i>Chem. Met. Eng.</i> , <b>26</b> , 209 (1922).
Oxidation of paraffins in gaseous phase.	Phosphates or borates.	Badische Anilin- und Soda Fabrik: B.P. 199,886 (1922).
Oxidation of paraffins in gaseous phase.	$V_2O_5$ .	Badische Anilin- und Soda Fabrik: U.S.P. 1,516,757 (1923).
Oxidation of paraffins in gaseous phase.	Nitrogen oxides.	Bibb: U.S.P. 1,547,725 (1923).
Oxidation of paraffins in liquid phase.	Zn stearate.	Winternitz and Teichner: B.P. 174,642 (1922).
Oxidation of paraffins in gaseous phase.	Nitrogen oxides.	Bibb and Lucas: <i>Ind. Eng. Chem.</i> , <b>21</b> , 633 (1929).
Oxidation of paraffins in liquid phase.	Mn stearate.	van Lier: P.P. 578,283 (1924).
Oxidation of paraffins, ceresine, Vaseline, paraffin oil and similar hydrocarbons; T. 160°.	Glass, porcelain, Cu, Fe, Mn, Al.	Badische Anilin- und Soda Fabrik: G.P. 405,850 (1924). P.P. 552,416 (1923).
Oxidation of paraffins in liquid phase.	Colloidal catalysts.	Caspari: B.P. 263,201 (1925).
Oxidation of paraffinic hydrocarbons.	Metallic soap catalysts.	Hebler: <i>Farben-Ztg.</i> , <b>32</b> , 1192–1194 (1926).
Oxidation of paraffins with $O_2$ to shellac-like artificial tars.	Mn oleate.	Alox Chemical Corporation: B.P. 309,384 (1927).
Oxidation of paraffins in liquid phase.	Organic compounds of alkaline-earth metals: Al and Mg; metal enolates; catalysts dissolved in fats + water vapor.	I.G. Farbenindustrie A.-G.: B.P. 310,069 (1927). B.P. 303,268 (1927).
Oxidation of paraffins in gaseous phase; saturated, aliphatic compounds, e.g., propane and butane, with more than one C atom in the molecule, in a mixture with $CH_4$ and $H_2O$ vapor at high temp. and pressures, using air, for the formation of aldehydes.	Oxides of high melting electro-negative metals with a low atomic volume and an atomic weight over 40 (graphic presentation of Lothar Meyer); contact time, less than 3 sec.	Byrnes: U.S.P. 1,858,095, May 10, 1932.
Oxidation of paraffins (lower) to alcohols at high pressure.		Wiesevich and Frolich: <i>Ind. Eng. Chem.</i> , <b>26</b> , 267 (1934).

Table 4 (Continued).

Reaction	Catalyst	Observer
Oxidation of paraffinic hydrocarbons (lower) with $H_2$ ; T. 250°, $C_2H_4$ formed. T. 300°, $C_2H_6$ formed.	$CuO$ , promoted by the addition of 2% $CoO$ , $NiO$ or $MnO$ (best); additions decrease the activity of the contact at high temp.	Pichler and Renkhoff: <i>Ges. Abhandl. Kenninis Kohle</i> , 12, 242-249 (1937).
Oxidation of high molecular paraffin hydrocarbons; temp. not above 115°; best oxidation at 98-112°; initial substance preheated to 150-160° before being subjected to the action of the oxidation gas with the accelerator.	Alkaline Mn cpds. containing Mn in the anion, for example, $NaMnO_4$ or $KMnO_4$ .	I. G. Farbenindustrie A.-G.: E. P. 478,317, Feb. 10, 1938.

Table 5. Catalytic Oxidation of Olefins (Ethylene).

Reaction	Catalyst	Observer
Oxidation of $C_2H_4$ with ozonized air and $H_2O$ vapor; T. 100°; yield, 70-80% $HCHO$ and 15-20% glycol.	Pumice, impregnated with alkali, $KMnO_4$ or $KClO_4$ .	Plauson: G.P. 344,615 (1921).
Oxidation of $C_2H_4$ to $HCHO$ ; T. 130°; yield, 2% by volume.	Osmium.	Wilstätter and Bommer: <i>Ann.</i> , 422, 36 (1921). Wilstätter and Bommer: G.P. 350,922 (1922).
✓ Oxidation of $C_2H_4$ to $HCHO$ ; T. 375°; yield, 85 parts by vol. $C_2H_4$ and 15 parts by vol. $O_2$ .	Boric acid or $H_2PO_4$ impregnated on burnt alumina.	Badische Anilin- und Soda Fabrik (Mittasch, Willfroth and Balz): G.P. 397,212 (1924). E.P. 199,886 (1923). F.P. 550,293 (1923).
Oxidation of $C_2H_4$ with $H_2O$ or $C_2H_5OH$ .	Pd black.	Fourneau and Ribas: <i>Bull. soc. chim.</i> , 4 (39), 587 (1926).
Oxidation of $C_2H_4$ ; no $HCHO$ formed.	Ag, Cu, Pd, or Pt on silicic acid gel.	Reyerson and Sweeringen: <i>J. Am. Chem. Soc.</i> , 50, 2872 (1928).
Oxidation of $C_2H_4$ ; T. 250-600°.	Silent electric discharge, $\alpha$ -radiation or ultraviolet light.	Dreyfus: F.P. 737,612, Dec. 14, 1932.
Oxidation of $C_2H_4$ .	Activated Ag + small amounts of Au, Cu and Fe.	Société Française de Catalyse Généralisée: F.P. 41,484, Jan. 10, 1933.
Oxidation of $C_2H_4$ to ethylene glycol; $CO_2$ added; diminished pressure.	Au, Cu and Fe.	Société Française de Catalyse Généralisée: F.P. 41,810, April 21, 1933. add to F.P. 729,952 (1932).
Oxidation of $C_2H_4$ .	Sb, Pb, Bi, Ag, Ni, Sn, or As, or their oxides.	Société Française de Catalyse Généralisée: F.P. 739,562, Jan. 13, 1933.
Oxidation of olefins with water vapor.	To the catalyst are added: glucose, molasses, starch, gelatin, pectin or higher alcohols which form true or colloidal solutions in water and which, on heating to 200°, leave in the catalyst only C.	Distillers Co., Ltd. (Joshua, Stanley and Dymock): Austrian P. 16,243, Sept. 20, 1934.
Oxidation of olefins, diolefins and cyclic hydrocarbons with $O_2$ (air) at high or diminished pressure; T. 250-600°.	Silent electric discharge, $\alpha$ -radiation or ultraviolet light.	Dupont (Leuter): U.S.P. 1,995,991, Mar. 26, 1935.
Oxidation of olefins with water vapor; T. 125-130°; 25-900 atm. pressure.	Volatile halide compounds: $HCl$ , $HI$ , $HBr$ or $CH_3Cl$ , $CCl_4$ , $NH_4Cl$ (I), etc., on pumice, silica gel, or coke.	Dupont: U.S.P. 2,014,740, Sept. 17, 1935.
Oxidation of $C_2H_4$ with water vapor; T. 325°; 700 atm. pressure.	Mo and Cr oxide.	Dupont (Carpenter): U.S.P. 2,008,348, July 16, 1935.
Oxidation of $C_2H_4$ to ethylene oxide; T. 300-400°.	Ag acetate, formate, or oxalate on active charcoal or silica gel.	N. V. de Bataafsche Petroleum Mij: E.P. 434,011, Sept. 19, 1935.
Oxidation of $C_2H_4$ with $O_2$ or $O_2$ -containing gases; T. 300-400°; normal, increased, or decreased pressure.	Product obtained by the decomposition of organic Ag cpds., e.g., oxalate, formate, or acetate; promoters: Cu, Au, Fe, Mn or Co, Ni, Cs, Th, Zn.	N. V. de Bataafsche Petroleum Mij: E.P. 434,011, Sept. 19, 1935.

Table 5 (Continued).

Reaction	Catalyst	Observer
Oxidation of unsaturated hydrocarbons by the oxidation products of $\text{H}_2\text{SO}_4$ , persulfuric acid, Caro's acid, $\text{H}_2\text{O}_2$ , $\text{O}_3$ , $\text{O}_2$ to alcohols, aldehydes, and acids; 30-80% $\text{H}_2\text{SO}_4$ is oxidized by an electric current.	$\text{CeSO}_4$ .	Hultmann and Powell Corp. (Hultmann): U.S.P. 1,992,309, Feb. 26, 1935.
Oxidation of $\text{C}_2\text{H}_4$ to ethylene oxide, $\text{C}_2\text{H}_4$ and $\text{CO}_2$ .	Activated charcoal serves to adsorb ethylene oxide which is then driven off by water vapor.	Société Française de Catalyse Généralisée: Ital. P. 347,086, Nov. 21, 1936.
Oxidation of $\text{C}_2\text{H}_4$ to ethylene oxide.	Special arrangement of the reaction chamber influences advantageously the streaming velocity, the turbulence of the gas mixture and the activity as well as the thickness of the catalyst.	Société Française de Catalyse Généralisée: F.P. 816,375, Jan. 15, 1937. E.P. 472,629, Oct. 28, 1937.
Oxidation of olefins with $\text{H}_2\text{O}$ to form aliphatic alcohols.	Heteropoly-acids and/or a salt thereof, silico-tungsten, boron-tungsten, phosphorus-tungsten, tungsten-arsenic acid; likewise iso-complex acids of W, Mo, V, Cr, S, Se, and Te; silica gel, kieselguhr, or adsorption charcoal may be used as carriers; a mixture with hydration catalysts, such as $\text{Al}_2\text{O}_3$ .	Carbide and Carbon Chemicals Corporation: F.P. 815,020, July 5, 1937.
Oxidation of $\text{C}_2\text{H}_4$ with $\text{O}_2$ or $\text{O}_2$ -containing gases.	Ag in a thin layer on tubes made of good conducting substances.	Distillers Co., Ltd. (Langwell, Maddocks and Short): F.P. 813,581, June 3, 1937. E.P. 466,416, June 24, 1937.
Oxidation of olefins with $\text{O}_2$ or $\text{O}_2$ -containing gases; T. 400-450°.	Finely divided Ag and/or Au, alloyed with small amounts of other metals.	Distillers Co., Ltd. (Langwell, Maddocks and Short): E.P. 462,487, April 8, 1937.
Oxidation of $\text{C}_2\text{H}_4$ to $\text{HCHO}$ ; T. 415-500°.	Mo, W, V, or Cr oxides on silica gel.	Smith Corporation (Hasche): U.S.P. 2,066,622 (1937).
Oxidation of unsaturated hydrocarbons with 30% $\text{H}_2\text{O}_2$ in homogeneous phase; the exothermic reaction occurs within an hour; in the case of difficultly oxidized cpds. oxidation is accelerated by light radiation; it is not certain whether true photocatalysis or only a strong light adsorption of the peracid occurs; possibly acetone, as a result of formation of unstable monomeric acetone peroxide, participates directly in the reaction mechanism; the reaction indicates an induction period; $\text{H}_2\text{O}_2$ however cannot be proved; the amount of reaction water permits the conclusion that $\text{H}_2\text{O}_2$ should react rather in the unsymmetrical form, $\text{OOH}_2$ , according to scheme (A) $\text{R} + \text{OOH}_2 = \text{RO} + \text{H}_2\text{O}$ , then in the symmetrical form, $\text{HOOH}$ , according to scheme (B) $\text{R} + \text{HOOH} = \text{R(OH)}_2$ ; as primary oxidation products are ascertained $\alpha$ -oxides and $\alpha$ -unsaturated alcohols; the yield of $\alpha$ -oxides is the higher, the more anhydrous the oxidation agent and the lower the reaction temp.; from chain olefins, $\alpha$ -oxide is always obtained, in a larger amount the greater the number of H atoms carried by the C atoms in the neighborhood of the double bond.	Pervanadic acid.	Treibs: <i>Ber.</i> , 72, 7-10 (1939).
Oxidation of ethylene.	Ag catalyst obtained by treating Ag or Ag cpds. with $\text{H}_2$ <i>in statu nascendi</i> ; for this purpose an Ag salt solution is electrolytically reduced or replaced by less noble metals, such as Zn or Al.	N. V. de Bataafsche Petroleum Mij.: E.P. 501,278, March 23, 1939.

Table 6. Catalytic Oxidation of Acetylene.

Reaction	Catalyst	Observer
Oxidation of $C_2H_2$ in liquid phase: $C_2H_2 + H_2O \rightarrow CH_3CHO$ .	Hg and its compounds in acid solutions.	Chemische Fabrik Griesheim-Electron A.-G. (Grünstein): G.P. 250,356 (1910).
Oxidation of $C_2H_2$ at low temperature: $C_2H_2 + H_2O \rightarrow CH_3CHO$ $CH_3CHO \rightarrow CH_3COOH$ .	Hg cpds. and oxidation catalysts in acid solutions.	Bayer: G.P. 297,442 (1913). Chemische Fabrik Griesheim-Electron A.-G. (Grünstein): G.P. 305,997 (1914).
Oxidation of $C_2H_2$ in vapor phase: $C_2H_2 + H_2O \rightarrow CH_3CHO$ $CH_3CHO \rightarrow CH_3COOH$ $2CH_3COOH \rightarrow (CH_3)_2CO + CO_2 + H_2O$ .	$Fe_2O_3$ ; hydrated Fe ores.	Rhenania Verein Chemische Fabriken: G.P. 365,285 (1913). G.P. 369,515 (1916). G.P. 379,596 (1916).
Oxidation of $C_2H_2$ in vapor phase: $C_2H_2 + H_2O \rightarrow CH_3CHO$ .	$MoO_3$ .	Deutsche Gold und Silber Scheideanstalt A.-G.: G.P. 334,357 (1916).
Oxidation of $C_2H_2$ with air and water vapor to $CH_3COOH$ ; T. 300–400°.	Mn or Cr vanadate on pumice.	Wohl: E.P. 154,579 (1920). refer also to Plauson: E.P. 156,152 (1920).
Oxidation of $C_2H_2$ in vapor phase: $C_2H_2 + H_2O \rightarrow CH_3CHO$ .	$ZnO + Cr_2O_3$ .	Badische Anilin- und Soda Fabrik: G.P. 415,686 (1923).
Oxidation of $C_2H_2$ in vapor phase: $C_2H_2 + H_2O \rightarrow CH_3CHO$ $CH_3CHO \rightarrow CH_3COOH$ $2CH_3COOH \rightarrow (CH_3)_2CO + CO_2 + H_2O$ .	$Fe_2O_3$ .	Deutsche Gold und Silber Scheideanstalt A.-G.: Aust. P. 88,631 (1917). Swiss P. 94,225 (1921).
Oxidation of $C_2H_2$ : $C_2H_2 + H_2O \rightarrow CH_3CHO$ $CH_3CHO \rightarrow CH_3COOH$ .	$ThO_2$ .	Lonza Elektrische Werke E.P. 192,392 (1923). F.P. 561,377 (1923).
Oxidation of $C_2H_2$ : (130 parts $C_2H_2$ , 80–100 parts $O_2$ ) T. 50–100°; $C_2H_2 + H_2O \rightarrow CH_3CHO$ $CH_3CHO \rightarrow CH_3COOH$ .	50 parts Hg nitrate, 10 parts $CeO$ .	Dreyfus: G.P. 409,947 (1925).
Oxidation of $C_2H_2$ .	$ZnO$ .	I.G. Farbenindustrie A.-G.: F.P. 299,048 (1929). F.P. 661,514 (1929).
Oxidation of $C_2H_2$ to glyoxal (oxalaldehyde); yield, 50%.	$N_2$ oxides act as transporters of $O_2$ .	Lenher: J. Am. Chem. Soc., <b>53</b> , 2962–2967 (1931).
Oxidation of $C_2H_2$ ; T. 400–410°; $2C_2H_2 + 3H_2O \rightarrow CH_3COCH_3 + CO_2$ .	200 g. highly active porous coal impregnated or covered with 35 g. iron-free Zn acetate and 10 g. Mn acetate.	Deutsche Gold und Silber Scheideanstalt A.-G. (Roessler, Walter and Schultz): G.P. 577,705, Kl 120, June 3, 1933.
Oxidation of $C_2H_2$ ; $2C_2H_2 + 3H_2O \rightarrow CH_3COCH_3 + CO_2$ .	Highly active charcoal charged with a mixture of Zn or Cd basic compounds, i.e., a mixture of alkalies or alkaline earths.	Deutsche Gold und Silber Scheideanstalt A.-G. (Roessler and Walter): G.P. 584,517, Kl 120, Sept. 21, 1933; add to G.P. 577,705 (1933).
Oxidation of $C_2H_2$ ; yield, 89% acetone.	$ZnO + (Fe_2O_3, Cr_2O_3, \text{ or } MnO)$ ; $ZnO : MnO = 4 : 1$ .	Uschakow and Rosengart: <i>Zhur. Khim. Prom.</i> <b>10</b> (4), 66–69 (1934).
Oxidation of $C_2H_2$ .	$2ZnO \cdot V_2O_5$ ; Cd vanadate.	Plotnikow, Plakidina and Weltistow: <i>Zhur. Obschei Khim.</i> <b>4</b> (66), 421–433 (1934).
Oxidation of $C_2H_2$ to $CH_3CHO$ ; T. 50–100°; elevated pressure may be used.	Hg salts in free acid; HgO or $HgSO_4$ in $H_2SO_4$ ; $Hg_2(PO_4)_2$ in $H_3PO_4$ , or $Hg_2(SO_4)_2$ in aromatic sulfonic acids.	Shell Development Co. (Millar and Steck): U.S.P. 2,005,946, June 25, 1935.
Oxidation of gases with comparatively low $C_2H_2$ content, using $H_2SO_4$ , to $CH_3CHO$ (10–30 times the amount of the salt solution is circulated in the reaction vessel per hour).	Iron sulfate solution containing Hg; the ratio of ferro- and ferri-sulfate is maintained constant so that more than 20% of the total amount of iron is in the ferri-form.	I. G. Farbenindustrie A.-G.: E.P. 466,569, June 24, 1937; add to E.P. 460,145, July 16, 1935. F.P. 478,812, July 31, 1936. F.P. 806,401 (Refer to C. 1937 I 2868).
Oxidation of $C_2H_2$ (arc) to $CH_3CHO$ (under favorable conditions, solid substances formed settle out).	Hg-containing Fe salt.	I.G. Farbenindustrie A.-G.: F.P. 815,717, July 21, 1937.



Table 6 (Continued).

Reaction	Catalyst	Observer
Oxidation of $C_2H_2$ with $H_2O$ to $CH_3CHO$ ; T. 200–500°.	Active C impregnated with an acid-acting catalyst, such as $H_3PO_4$ or $H_2PO_4$ , and a metal: Zn, Cd, or Ag.	Deutsche Gold und Silber Scheideanstalt A.-G. (Roessler and Walter); U.S.P. 2,098,842, Nov. 9, 1937.
Oxidation of $C_2H_2$ to acetaldehyde; the reaction temp. is held at the critical point or as close to the critical point of the catalyst surface in the streaming gas as is possible.	The catalyst surface is made by adding metallic Hg to dilute acids substituted by oxidation agents.	I. G. Farbenindustrie A.-G. (Roth, Elvert and Steinberger) G.P. 672,480, Kl 120, March 4, 1939.
Oxidation of $C_2H_2$ .	Cd or Cr + $ThO_2$ .	
Oxidation of $C_2H_2$ .	W acid + Mo acid or V acid in an Al contact tube.	

Table 7. Catalytic Oxidation of Methanol.

Reaction	Catalyst	Observer
Oxidation of $CH_3OH$ to $HCHO$ using air.	Glowing Pt spiral.	Hofmann: <i>Ann.</i> , 145, 357 (1868); 176, 129 (1875). Farbenfabrik vorm Meister Lucius Bruning (Trillat): G.P. 55,176 (1889).
Oxidation of $CH_3OH$ to $HCHO$ .		Fabrik Merklin A.-G. (Tollens and Loew): (1882).
Oxidation of $CH_3OH$ .	Pt on asbestos.	Farbenfabrik vorm Meister Lucius Bruning (Trillat): G.P. 55,176 (1889).
Oxidation of $CH_3OH$ .	Ag on asbestos.	Blank: G.P. 228,697 (1908).
Oxidation of $CH_3OH$ to $HCHO$ , using air passed at 53–54°; reaction gas cooled at 41–42°; 40% $HCHO$ dissolved.	Cu tubes.	Orloff: "Formaldehyde," Leipzig, 1909. Menzel: "Formaldehyde," Leipzig, 1927.
Oxidation of $CH_3OH$ to $HCHO$ .	Cu, Cu/Ag.	Fokin: <i>J. Russ. Phys.-Chem. Soc.</i> , 45, 286 (1913).
Oxidation of $CH_3OH$ to $HCHO$ ; yield, 79%.	Cu + Pt.	
Oxidation of $CH_3OH$ to $HCHO$ ; yield, 70%.	Cu.	Legg and Adam: B.P. 166,249 (1919). U.S.P. 1,418,448 (1921).
Oxidation of $CH_3OH$ to $HCHO$ ; yield, 86.8–87.4%.	Cu wire net in the form of a cylinder, 10 cm. $\times$ 16 mm.	Commercial Solvents Corp.: U.S.P. 1,576,544 (1924).
Oxidation of $CH_3OH$ .	$ThO_2$ + Cu.	Holzverkohlung A.-G.: G.P. 402,849 (1924).
Oxidation of $CH_3OH$ to $HCHO$ ; yield, 96%.	Ag + Pt.	Holzverkohlung A.-G.: G.P. 402,849 (1924). F.P. 467,076.
Oxidation of 100 parts $CH_3OH$ to $HCHO$ ; yield, (1) 71%, (2) 64–66%, (3) 43–47%.	(1) Au on asbestos. (2) Ag on asbestos. (3) Cu on asbestos.	Fokin: refer to Sabatier: "Die Katalyse in der Organischen Chemie," 2nd Ed., Leipzig, 1927.
Oxidation of $CH_3OH$ to $HCHO$ .	Glowed charcoal + active charcoal.	Fabrique de Produits Chimique (Kala and Khartschew): F.P. 620,754 (1927).
Oxidation of $CH_3OH$ to $HCHO$ .	Mo and Fe oxide mixtures (Fe oxide alone, poor catalyst).	Adkins and Peterson: <i>J. Am. Chem. Soc.</i> , 53, 1512–20 (1931).
Oxidation of $CH_3OH$ to $HCHO$ ; T. 225–300°; yield, almost quantitative without formation of side products such as $HCOOH$ .	$MoO_3$ + one or more oxides of Fe, La, Th, Nb, Zn, Sn, V; (1) 40% $MoO_3$ 45% $V_2O_5$ 15% $Fe_2O_3$ , or (2) 50% $MoO_3$ 40% $V_2O_5$ 10% $FeO$	Bakelite Corporation: E.P. 381,570, Nov. 3, 1932.
Oxidation of $CH_3OH$ .	$Fe_2O_3$ , $FeO$ , or $MoO_3$ .	Natta: <i>Giorn. chim. ind. applicata</i> , 14, 545–551 (1932).

Table 7 (Continued).

Reaction	Catalyst	Observer
Oxidation of $\text{CH}_3\text{OH}$ to $\text{HCHO}$ ; yield, 75%.	Ag.	Marek and Hahn, Dorothy: "Catalytic Oxidation of Organic Compounds in the Vapor Phase," ch. III, V, Chemical Catalog Co. (Reinhold Publishing Corp.), New York, 1932.
Oxidation of $\text{CH}_3\text{OH}$ to $\text{HCHO}$ .	Heavy metal oxides and base exchanging bodies on kieselguhr.	Selden Corporation (Jaeger): U.S.P. 1,935,054 (1933).
Oxidation of $\text{CH}_3\text{OH}$ to $\text{HCHO}$ .	Porous, inert materials, such as asbestos and porcelain, are impregnated with $\text{AgNO}_3$ treated with dilute $\text{HCOOH}$ .	Société Anonyme Chimique Mildé Fils et Cie: Swiss P. 169,857, Sept. 17, 1934.
Oxidation of $\text{CH}_3\text{OH}$ to $\text{HCHO}$ ; by regulating the conc. of $\text{O}_2$ , it is possible to decrease the influence of side reactions, namely, further oxidation of $\text{CH}_3\text{OH}$ to $\text{CO}_2$ and decomposition of $\text{HCHO}$ ; increasing $\text{O}_2$ from 52% to 110% decreases the yield of $\text{HCHO}$ from 93% to 57% (losses due to oxidation of $\text{CH}_3\text{OH}$ to $\text{CO}_2$ ); with catalyst (1), 1.6-1.8 l. of air are passed/min.; (2), 1.2-1.31 l. of air are passed/min.	(1) Cu wire gauze in the form of a cylinder, 10 cm. $\times$ 16 mm.; yield, $\text{HCHO}$ , 86.8-87.4% with an $\text{O}_2$ conc. 50-55% of the theoretical value; (2) Cu wire plated with Ag; yield, $\text{HCHO}$ 92.7-93.2% with an $\text{O}_2$ conc. 52-57% of the theoretical value; (3) Ag on pumice; yield, $\text{HCHO}$ up to 90% with an $\text{O}_2$ conc. of 50% of the theoretical value.	Gurewitsch and Tschirwinskaja: <i>Zhur. Khim. Prom.</i> , 12, (1), 57-61 (1935).
Oxidation of $\text{CH}_3\text{OH}$ to $\text{HCHO}$ ; yield, 5.2%.	Pt.	
Oxidation of $\text{CH}_3\text{OH}$ .	Cu + 0.1% Ce (space velocity 800 at 200°C.). Cu + Th (space velocity less effective, 900 at 205°C.).	
Oxidation of methanol to formaldehyde; a parallel is drawn between adsorption and catalytic activity; two similar curves are obtained at 360° for adsorption of the amount of $\text{H}_2$ as a function of the composition of the catalyst and the percentage of methanol decomposition against the composition of the catalyst.	Zn-Cr (with up to 80 atoms of zinc, a definite activated adsorption between (300 and 350°) is obtained).	Rumford: <i>J. Roy. Tech. Coll. (Glasgow)</i> , 4, 427-40 (1939).

Table 8. Catalytic Oxidation of Ethanol.

Reaction	Catalyst	Observer
Oxidation of ethanol to acetaldehyde.	Pt suboxide and Pt black.	Debereiner: <i>Jahresber.</i> , 3, 162 (1823).
Oxidation of ethanol to acetaldehyde; T. 150-300°.	Charcoal.	Calvert: <i>J. Chem. Soc.</i> , 20, 293 (1867).
Oxidation of ethanol to $\text{CH}_3\text{COOH}$ .	Carbon saturated with $\text{O}_2$ .	Calvert: <i>Compt. rend.</i> , 64, 1246 (1867).
Oxidation of ethanol.	Light metals or Cu on pumice or asbestos.	Glock: G.P. 109,015 (1899). Bayer: G.P. 346,520 (1917).
Oxidation of ethanol to $\text{CH}_3\text{COOH}$ in the vapor phase.	Ag on brown coal, on pitch and on charcoal.	Demestedt and Hassler: G.P. 203,848 (1907).
Oxidation of ethanol to $\text{CH}_3\text{COOH}$ .	Xylene.	Clamician and Silber: <i>Ber.</i> , 46, 3894 (1912).
Oxidation of ethanol.	Ru and its compounds.	Badische Anilin- und Soda Fabrik: G.P. 275,518 (1913).
Oxidation of ethanol; T. 250-350°.	Metal contact finely dispersed on ton.	Industrial Alcohol Co. (Backhaus and Arentz): U.S.P. 1,388,841 (1921).
Oxidation of ethanol to acetaldehyde.	Benzoquinone; natural bleaching earth acts better than charcoal.	Gurewitsch: <i>Z. physik. Chem.</i> , 107, 235 (1923).
Oxidation of ethanol to acetaldehyde at room temp.	Bone charcoal treated with iodine.	Firth and Watson: <i>Trans. Faraday Soc.</i> , 20, 370 (1924).

Table 8 (Continued).

Reaction	Catalyst	Observer
Oxidation of ethanol to HCHO; T. 520-530°; yield, 50%.	Melted boric acid on silicic acid gel or kieselguhr.	Badische Anilin- und Soda Fabrik; G.P. 397,212 (1924).
Oxidation of ethanol to acetalde- hyde; yield, 90-93% $2\text{CH}_3\text{CH}_2\text{OH} + \text{O}_2 \rightarrow$ $2\text{CH}_3\text{CHO} + 2\text{H}_2\text{O}$	Ag wire gauze (red glow).	Holzverkohlungs Industrie A.-G.: G.P. 422,729, Kl 120, Dec. 10, 1925.
Oxidation of ethanol with $\text{H}_2\text{O}_2$ .	Ferric ion.	Walton and Christensen: <i>J. Am.</i> <i>Chem. Soc.</i> , <b>48</b> , 2083-2091 (1926).
Oxidation of ethanol.	$\text{V}_2\text{O}_5$ on silicic acid gel or natural bleaching earth.	Fester and Berraz: <i>Anales asoc.</i> <i>quim. argentina</i> , <b>15</b> , 210-215 (1927).
✓ Oxidation of ethanol.	$\text{V}_2\text{O}_5$ , $\text{UO}_2$ , $\text{MoO}_3$ .	Barrett Co.: U.S.P. 1,636,952 (1927).
Oxidation of ethanol to $\text{CH}_3\text{COOH}$ .	Ag.	Goldschmidt: E.P. 290,523 (1927). U.S.P. 1,666,447 (1928).
Oxidation of ethanol to $\text{CH}_3\text{COOH}$ .	Ag.	Holzverkohlungs Industrie A.-G.: E.P. 294,037 (1927).
Oxidation of ethanol.	$\text{V}_2\text{O}_5$ .	Fester and Berraz: <i>Anales asoc.</i> <i>quim. argentina</i> , <b>15</b> , 210-215 (1927).
Oxidation of ethanol.	Asbestos impregnated with $\text{Na}_2\text{PtCl}_6$ solution.	Dabietos and Makris: <i>Praktika te</i> <i>Akad. Athenon</i> , <b>3</b> , 569 (1928).
Oxidation of ethanol.	Pt metals.	Müller and Schwabe: <i>Kolloid-Z.</i> , <b>52</b> , 163-173 (1930).
Oxidation of ethanol.	$\text{CuO}$ ; rare earths, $\text{Sm}_2\text{O}_3$ .	Day: <i>J. Phys. Chem.</i> , <b>35</b> , 3272- 3279 (1931).
Oxidation of ethanol; T. 250°.	$\text{C} + \text{Cu} = 1.5 : 2.1$ ; Cu prepared from $\text{Cu}(\text{OH})_2$ or $\text{CuCO}_3$ .	Martineau: <i>Compt. rend.</i> , <b>193</b> , 1189-1192 (1931).
Oxidation of ethanol to acetalde- hyde; T. 210-441°; pressure, 1-50 atm.; yield, 78.6%; (1) T. 359-411° (2) T. 355-394°	(1) Ag + 0.14% $\text{Sm}_2\text{O}_3$ (2) Ag + 0.27% $\text{Sm}_2\text{O}_3$	Day: <i>J. Phys. Chem.</i> , <b>35</b> , 3272- 3279 (1931).
Oxidation of ethanol; T. 250°.	Active charcoal and $\text{CuO}$ into which a small amount of $\text{NH}_3$ has been stirred.	Martineau: <i>Compt. rend.</i> , <b>193</b> , 1189-1192 (1931).
Oxidation of ethanol to acetalde- hyde and 25-27% acetic acid.	$\text{CuO}$ on silicic acid gel contain- ing Ag, Co or $\text{ZnO}$ , $\text{MnO}_2$ (at a low temp., active catalysts).	F.P. 707,132 (1931); (Refer to C. 1931 II 3156).
Oxidation of ethanol.	Molten $\text{NaNO}_3$ and $\text{KNO}_3$ (for partial oxidation, a "Pyrex" tube in air, a "Pyrex" tube in a salt bath, and a Cu glass sealed chamber is used).	Keyes and Faith: <i>Eng. Exp. Sta.</i> <i>Bull. No. 252</i> , 2 (1932).
Oxidation of ethanol.	$\text{C} + \text{ZrO}_2$ ( $\text{ThO}_2$ ) $\text{C} + \text{Cr}_2\text{O}_3$ ( $\text{ThO}_2$ ) $\text{C} + \text{Cu} + \text{ZrO}_2$ ( $\text{ThO}_2$ ) (this ternary mixture acts at 63°, while the binary mixture, $\text{Cu} + \text{C}$ , accelerates oxidation below 100°).	Martineau: <i>Compt. rend.</i> , <b>194</b> , 1350 (1932).
Oxidation of ethanol.	Ag and Cu.	Dreyfus: E.P. 390,847, May 11, 1933.
Oxidation of ethanol.	$\text{Fe}_2\text{O}_3$ (pH=0.7; depends on the anion of the Fe salts; catalytic action decreases with increase in pH; pH a maximum for Cl ion).	Goldschmidt and Paunz: <i>Ann.</i> , <b>502</b> , 1-19 (1933).

Table 8 (Continued).

Reaction	Catalyst	Observer
Oxidation of ethanol; T. 210-441; pressure, 1-50 atm.; T. 359-411°; T. 355-394°; the aldehyde yield decreases with: (1) increasing pressure, and (2) prolonged contact time; the first factor influences the primary reaction; the second, the secondary reaction; yield with mixed catalyst up to 78.6%; gives maximum at 540°.	Ag.  Ag + 0.14% Sm <sub>2</sub> O <sub>3</sub> Ag + 0.27% Sm <sub>2</sub> O <sub>3</sub> (Activity remains constant); 1-5% Sm <sub>2</sub> O <sub>3</sub> causes a decrease in activity.	Patterson and Day: <i>Ind. Eng. Chem.</i> , <b>26</b> , 1276-1279 (1934).
Oxidation of ethanol to acetaldehyde; T. 400-450°; yield, 94%.	Cu or Ag wire gauze.	Kagan: <i>Trudy Vsesoyuz. Mendeleevskogo S'ezda</i> , (6th Congr.) <b>2</b> (Part 1), 739-745 (1935).
Oxidation of ethanol; T. 300°, vertical tube; T. 450°, horizontal tube; T. 500° maximum yield obtained at these temperatures.	Cu.  Ag + Cu = 4 : 1.	Costeana and Coşosinschi: <i>Bul. Facult. Stiint. Cernauti</i> , <b>10</b> , 392-400 (1936).
Oxidation of ethanol.	Electrically heated Cu tube in which a Pt spiral catalyst is fixed axially.	Coşosinschi: <i>Z. Elektroch.</i> , <b>42</b> , 876-879 (1936).
Oxidation of alcohol to acetaldehyde; T. 550-650°.	Ag (dehydrogenating)	Neumann and Lush: E.P. 502,725, April 20, 1939.

Table 9. Catalytic Oxidation of Higher Alcohols.

Reaction	Catalyst	Observer
Oxidation of amyl alcohol to valeric acid.	Charcoal.	Calvert: <i>J. Chem. Soc.</i> , <b>5</b> , 293 (1867).
Oxidation of <i>n</i> -butyl alcohol with air in water vapor to butyraldehyde; T. 280-320°; yield, 75%.	CuO (from melted CuO reduced at 200° with H <sub>2</sub> ).	Legg and Adam: E.P. 173,004 (1922).
Oxidation of isopropyl alcohol to acetone; T. 425-480°; yield, 75% yield, 60% yield, 55% $2\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + \text{O}_2 \rightarrow 2\text{CH}_3\text{COCH}_3 + 2\text{H}_2\text{O}$	Cu. Fe filings plated with Cu. Steel wool.	Hunt: U.S.P. 1,365,053 (1920). U.S.P. 1,479,817 (1923). E.P. 173,539 (1922).
Oxidation of isopropyl alcohol to acetone; yield, 80%.	Zn phosphide.	I. G. Farbenindustrie A.-G.: E.P. 263,877 (1927).
Oxidation of secondary alcohols: a mixture of isopropyl alcohol and <i>sec</i> -butyl alcohol or amyl alcohol; T. 225-325°.	Finely dispersed Cu on ton or kaolin.	Standard Alcohol Co. (Cardarelli): U.S.P. 1,988,481 (1935).

Table 10. Catalytic Oxidation of Other Alcohols.

Reaction	Catalyst	Observer
Oxidation of cyclic alcohols: borneol to camphor; 100 parts isoborneol dissolved in 10 parts xylene to camphor; yield, 97-98%.	5 g. Active charcoal or graphite and 5 g. Ca hydrate.	Gammay: F.P. 627,845 (1927).
Oxidation of polyvalent alcohols with H <sub>2</sub> O <sub>2</sub> .	Fe salts (in an acid medium).	Kuchlin and Boeseken: <i>Rec. trav. chim.</i> , <b>47</b> , 104-126 (1928).
Oxidation of benzyl alcohol to benzoic acid; T. 300°.	Active silicic acid.	I. G. Farbenindustrie A.-G. (Mitsch and Luther): G.P. 520,828 (1931).
Oxidation of unsaturated primary or secondary alcohols, having at least four C atoms, with O <sub>2</sub> ; T. 300-550°.	Cu or elements of the 3rd group of the Periodic System.	N. V. de Bataafsche Petroleum Mij. (Groll and de Jong): E.P. 436,840, November 14, 1935. F.P. 788,921, October 19, 1935.

Table 10 (Continued).

Reaction	Catalyst	Observer
Oxidation of primary and secondary ketone alcohols (ketols) with free $O_2$ to diketones.	Ti, Cr, Mn, Fe, Co, Ni, Se, Cu, Zn, V cpds. and their mixtures; free Cu, Ag; bronze; Ag-Zn alloy; Ag-As alloy; Au, Au-Ag alloy.	Shell Development Co. (de Simo and McAllister): U.S.P. 2,043,950, June 9, 1936.
Oxidation of unsaturated alcohols having the general formula: $R-\overset{\text{X}}{\underset{ }{\text{C}}}-\text{CHOH}$ , where R is an alkyl radical with a double bond in the middle and X is hydrogen; e.g., cinnamic alcohol to cinnamic aldehyde; T. 450°; yield, 85%; 240 cc. cinnamic alcohol to one cu. ft. $O_2$ per hour.	Metallic Ag ( $O_2$ transporting catalysts). Ni wire gauze.	Shell Development Co. (Groll and de Jong): U.S.P. 2,042,220 (1936).

Table 11. Catalytic Oxidation of Acetaldehyde.

Reaction	Catalyst	Observer
Oxidation of $C_2H_4O$ to acetic acid.	$CeO_2$ (1%); Pt black.	Mulder: <i>Rec. trav. chim.</i> , 2, 47 (1883).
Oxidation of $C_2H_4O$ to acetic acid.	$V_2O_5$ , $UO_2$ .	Chemische Fabrik Griesheim-Elektron A.-G. (Grunstein): G.P. 261,589 (1911).
Oxidation of $C_2H_4O$ in a solution of glacial acetic acid and tetrachlorethane to acetic acid; T. 70-80°; pressure 1-2 atm. (industrial process).	Mn salts of organic acids (0.1% of the amount of aldehyde) e.g., Mn acetate, formate, butyrate, benzoate or lactate.	Verein für Chemische Industrie (Mainz): G.P. 301,274 (1917). Konsortium für Elektrochemische Industrie: G.P. 305,550 (1918).
Oxidation of $C_2H_4O$ .	Kieselguhr.	Dreyfus: G.P. 299,782 (1917).
Oxidation of $C_2H_4O$ .	Platinized asbestos.	Dreyfus: F.P. 487,412 (1918).
Oxidation of $C_2H_4O$ .	Ni acetate.	Badische Anilin- und Soda Fabrik: G.P. 294,727 (1919).
Oxidation of $C_2H_4O$ to acetic acid.	Cpds. of Fe + alkali salts or organic acids.	Badische Anilin- und Soda Fabrik: G.P. 296,282 (1917).
Oxidation of $C_2H_4O$ ; T. 10-20°; pressure 5-10 atm.	Ca phosphate, kaolin, bone ash.	Dreyfus: B.P. 157,307 (1920). B.P. 154,680 (1920).
Oxidation of $C_2H_4O$ .	$Fe_2O_3$ + Na acetate.	Dreyfus: B.P. 156,916 (1920).
Oxidation of $C_2H_4O$ without a solvent and air blown in to acetic acid; T. 10-20° pressure 5-10 atm. $CH_3CHO + O_2 \rightarrow CH_3CO_2H$ $CH_3CO_2H + CH_3CHO \rightarrow 2CH_3COOH$ (intermediate formation of peracetic acid).	Bone charcoal, ash, or artificial Ca phosphate. Kaolin.  Kieselguhr.  $Fe_2O_3$ -Na acetate mixture.	Dreyfus: B.P. 154,680 (1920). British Cellulose and Chemical Mfg. Co.: E.P. 154,304 (1920). Farbenfabriken vorm Friedrich Bayer & Co.: G.P. 299,782 (1928). Aust. P. 89,924 (1922). Dreyfus: E.P. 156,196 (1920).
Oxidation of $C_2H_4O$ to acetic acid.	Mn, Ce, Mo, V salts accelerate electrolysis.	Société des Acières et Forges de Firminy: Swiss P. 88,186 (1920).
Oxidation of $C_2H_4O$ .	$V_2O_5$ .	Sealione and Frazer: E.P. 166,285, Aug. 11, 1921.
Oxidation of $C_2H_4O$ to acetic acid.	Cu acetate.	U.S.P. 1,375,345, April 19, 1921.

Table 11 (Continued).

Reaction	Catalyst	Observer
Oxidation of $C_2H_4O$ with $O_2$ or air to acetic acid.	Kieselguhr (not necessary to add acid to the initial aldehyde with the use of this catalyst).	Farbenfabriken vorm. Friederich Bayer & Co.: Aust. P. 89,924 (1922). G.P. 299,782 (1917).
Oxidation of $C_2H_4O$ to $CH_2O$ .	Metals or metal oxides: $V_2O_5$ or $CeO$ ; addition of water vapor or inert gases accelerate reaction.	Konsortium für Elektrochemische Industrie: Swiss P. 100,179 (1923). E.P. 178,842 (1922). U.S.P. 1,460,244 (1923). F.P. 550,236 (1923).
Oxidation of $C_2H_4O$ to acetic acid; T. $10-20^\circ$ ; pressure 5-10 atm.	A mixture of Co and Cr acetate (without a solvent).	Chemische Fabriken Worms: Swiss P. 100,180 (1923).
Oxidation of $C_2H_4O$ to acetyl peroxide and glacial acetic acid.	Co acetate dissolved in glacial acetic acid or a tertiary base, such as pyridine.	Konsortium für Elektrochemische Industrie: G.P. 403,052 (1924).
Oxidation of $C_2H_4O$ without a solvent; T. $10-20^\circ$ ; pressure 5-10 atm.	$CaPO_4$ , bone ash, kaolin, kieselguhr, mixture of $Fe_2O_3$ with Na acetate.	Dreyfus: E.P. 299,782 (1928). E.P. 156,916 (1920).
Oxidation of $C_2H_4O$ with air to acetic acid.	Organic salts plus active charcoal; finely powdered bone charcoal plus 10 parts sodium acetate.	Badische Anilin- und Soda Fabrik: G.P. 296,282 (1928).
Oxidation of $C_2H_4O$ with air or $O_2$ in a 20% aqueous solution of the catalyst; T. $30-40^\circ$ .	Co acetate, 0.005% Co acetate, 0.002% Mn acetate, 0.2%.	Imperial Chemical Industries, Ltd.: E.P. 304,350, Feb. 14, 1929.
Oxidation of $C_2H_4O$ to acetic acid; T. $90^\circ$ ; yield, 90%; addition of a dilute $NaNO_3$ solution to the purified silica aerogel increases the yield of acetic acid and Na ions prevent formation of side reactions; at high temp. only a moderate conversion takes place.	Commercial silica aerogel; purified silica aerogel, active when amorphous and inactive when crystalline; strongly adsorbent, but when covered with a non-adsorbent layer, becomes inactive; activity destroyed by Pt and V; impregnated with Mn salts and Cr, Cu, W oxides; impregnation with 19% $Al_2O_3$ and 8.8% Ni tartrate acts favorably; metallic Cu, active charcoal, Al, Pt and V on pumice, inactive at low temp.; at high temp., more $CO_2$ than $CH_3COOH$ formed.	Burton: <i>Chem. Age (London)</i> , 31, 169 (1934). Kistler, Swain and Appel: <i>Ind. Eng. Chem.</i> , 26, 388-91 (1934); (Refer to C. 1934 II 1817).
Oxidation of $C_2H_4O$ to acetone.	A mixture of hydroxides precipitated by $NH_4OH$ from $Cr(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ alone or with alkaline earths; oxides of Mn, Fe, Cu, Ni, Zn with halides of these metals; carbonates, such as $CuCO_3$ .	Commercial Solvents Corporation (Swallen): U.S.P. 1,970,782, Aug. 21, 1934.
Oxidation of $C_2H_4O$ .	Mn acetate + Mn nitrate (continuous process).	Kasarnowski and Feigin: <i>Zhur. Khim. Prom.</i> 12, 150-156 (1935).
Oxidation of $C_2H_4O$ .	Mn.	Kagan and Lubarsky: <i>J. Phys. Chem.</i> , 39, 837-846 (1935); refer also to Milas and McAlevy: <i>J. Am. Chem. Soc.</i> , 56, 1221-25 (1934); (Refer to C. 1934 II 441).
Oxidation of $C_2H_4O$ with $O_2$ in hexane and $Cl_4$ ; amounts bound to oxygen as per-acids are different for different solvents; hexane has an especially strong influence; action of $O_2$ on $CH_2O$ in these solvents is extremely small, almost zero; $C_2H_4O$ on the other hand is considerably influenced catalytically by the catalyst $O_2$ .	$O_2$ (strong differences for single solvents with regard to the chain reaction in which $O_2$ acts as an accelerator of the auto-oxidation).	Briner and Lardon: <i>Helv. Chim. Acta</i> , 19, 850-857, July 1, 1936.

Table 12. Catalytic Oxidation of Butyraldehyde.

Reaction	Catalyst	Observer
Oxidation of butyraldehyde; T. 35-40°.	Mn butyrate.	Chemische Fabrik Griesheim-Elektron A.-G. (Grünstein): G.P. 27,368.
Oxidation of butyraldehyde to butyric acid.	Mn butyrate on chamotte.	Legg and Adam: E.P. 173,004 (1920). U.S.P. 1,418,448 (1921).
Oxidation of butyraldehyde with air or other oxygen-containing gas to butyric acid; T. 650°; yield 80%.	Mn butyrate on pumice or alumina.	Commercial Solvents Corporation: U.S.P. 1,418,448 (1922). F.P. 543,569 (1922). Can. P. 249,868 (1924).
Oxidation of butyraldehyde to butyric acid; T. 65°; yield 80%.	Mn butyrate on ton pieces.	Commercial Solvents Corporation: U.S.P. 1,418,448 (1922). U.S.P. 1,580,137 (1926).
Oxidation of croton aldehyde with air or other O <sub>2</sub> -containing gas to crotonic acid; T. 40°.	Mn salts.	Elektrizitätswerke-Lonza Chemische Fabrik A.-G.: Swiss P. 88,560 (1920). F.P. 536,424 (1922). (Refer to C. 1922 IV 799R). U.S.P. 1,445,544 (1923).
Auto-oxidation of butyraldehyde in isooctane (deoxygenation of air by heating to 800-850° causes it to lose its oxidation action).	O <sub>2</sub> (even in highly diluted state accelerates auto-oxidation processes; the catalytic action increases with increasing dilution of O <sub>2</sub> ).	Briner: <i>Atti Congr. intern. chim., 10th Congr., Rome, 2</i> , 175 (1938).

Table 12a. Catalytic Oxidation of Various Aldehydes.

Reaction	Catalyst	Observer
Catalytic oxidation (combustion) of CH <sub>3</sub> O in air; due to fast polymerization of CH <sub>3</sub> O on metallic surfaces the experiments are carried out in glass vessels; for small conc. of CH <sub>3</sub> O the heating velocity of the wire is proportional to the CH <sub>3</sub> O conc; if the content rises to 20-65%, an explosion takes place after the surface reaction has started; at still higher conc. a homogeneous oxidation simultaneously takes place; if the aldehyde content is higher than 85%, the heterogeneous reaction is suppressed; it is postulated that the presence of adsorbed O <sub>2</sub> is of great significance in surface combustion.	Pt wire.	Davies: <i>Proc. Leeds Phil. Lit. Soc. Sci. Sect.</i> , <b>3</b> , 300-304 (1937).
Oxidation of ketones and aldehydes according to the scheme: $RCH_2COCH_3 + SeO_2 \rightarrow RCO-COCH_3 + H_2O + Se$ . Oxidation of acetals was found to be considerably slower than that of ketones or aldehydes, and because an induction period precedes their oxidation it is concluded that the reaction passes through the enolic form; besides the main reaction, simultaneously occurs the formation of Se organic compounds and further oxidation of the primarily formed diketones and ketone aldehyde, which as is known take the enolic form more readily than the monoketones, and thus can be faster oxidized by SeO <sub>2</sub> ; this oxidation reaction of ketones by SeO <sub>2</sub> may be used for following the relative enolization of ketones and aldehydes from the magnitude of the oxidation velocity.	SeO <sub>2</sub> or H <sub>2</sub> SeO <sub>3</sub> .	Melnikow and Rokitzkaja: <i>Zhur. Obshchei Khim.</i> , <b>7</b> , (69), 2738-2747 (1937).

Table 13. Catalytic Oxidation of Various Acids.

Reaction	Catalyst	Observer
Oxidation of oxalic acid solutions.	Manganous salts.	Jorissen and Reicher: <i>Z. physik. Chem.</i> , <b>31</b> , 142 (1900).
Oxidation of carbonic and formic acids to CO <sub>2</sub> .	Charcoal.	Freundlich: <i>Ibid.</i> , <b>57</b> , 458 (1907).
Oxidation of oxalic acid.	Sugar and blood charcoal.	Warburg: <i>Biochem. Z.</i> , <b>136</b> , 266 (1923).
Oxidation of maleic acid to glyoxylic acid, CO <sub>2</sub> and H <sub>2</sub> O.	Sugar charcoal.	Rideal and Wright: <i>J. Chem. Soc.</i> , <b>127</b> , 1347 (1925).
Oxidation of dioxymaleic acid (unsaturated dicarbonic acid).	Fe (reaction retarded by fluorides).	Lipmann: <i>Biochem. Z.</i> , <b>206</b> , 171-185 (1928).
Oxidation of oxalic acid by KMnO <sub>4</sub> .	Fe (reaction retarded by fluorides).	Lipmann: <i>Ibid.</i> , <b>206</b> , 171-185 (1928).
Oxidation of acetic and propionic acids.		Compel, Mayer and Wurmser: <i>Compt. rend.</i> , <b>178</b> , 1025 (1923).
Oxidation of formic acid with H <sub>2</sub> O <sub>2</sub> .	Fe <sup>+++</sup> hydroxides; the hydroxide under action of H <sub>2</sub> O <sub>2</sub> is converted into the peroxide and the latter reacts with formic acid; the activity of the catalyst is due to the presence of active H <sub>2</sub> found especially where OH groups bound to the Fe atom are present; the Fe hydroxides presumably occupy a separate place as catalysts with respect to other metals, because the latter form hydroxides rather than oxyhydrates, and therefore have no active H <sub>1</sub> .	Krause and Gawrychowa: <i>Ber.</i> , <b>70</b> , 439-443 (1937).
Oxidation of acetic acid (similar to lactic acid) and other aliphatic acids with H <sub>2</sub> O <sub>2</sub> ; 1/200N CH <sub>3</sub> COOH requires 105 hrs. 1/20N CH <sub>3</sub> COOH requires about 30 days.	0.2 g. orthoferrihydroxide; Fe <sup>+++</sup> form has strong dehydrogenating action upon the organic substances and oxidizes them; Fe <sup>+++</sup> hydroxide is rebuilt thereby.	Krause and Jankowski: <i>Ber.</i> , <b>70</b> , 1744-1749 (1937).
Oxidation of butyric acid with H <sub>2</sub> O <sub>2</sub> .	Co + K phosphate better than Co + Na phosphate; monoalkali phosphates; MnO <sub>2</sub> together with H <sub>3</sub> PO <sub>4</sub> or H <sub>2</sub> SO <sub>4</sub> .	Witzemann: <i>J. Am. Chem. Soc.</i> , <b>48</b> , 202-208 (1926); <b>52</b> , 640-646 (1930).
Oxidation of β-oxybutyric acid.	Fuller's earth.	Ruck: <i>Akad. Wiss. Wien</i> , <b>70</b> , 98 (1933).
Oxidation of amino-acids.	O <sub>2</sub> .	Bergel and Boltz: <i>Z. physiol. Chem.</i> , <b>220</b> , 20-26 (1933).
Catalytic conversion of thiosulfuric acid in polythionic acid.	Addition of Na <sub>2</sub> HAsO <sub>4</sub> solution accelerated by SO <sub>2</sub> in the presence of HCl; SbCl <sub>3</sub> weak acting; BiCl <sub>3</sub> very weak acting.	Kurtenacker and Ivanow: <i>Z. anorg. allgem. Chem.</i> , <b>185</b> , 337-359 (1930).
Oxidation of 0.1N, 0.05N, and 0.025N aqueous solution of oxalic acid; in the case of the red solution, the reaction proceeds monomolecularly after an induction period, as well as a transition period; in the case of the black solution, the induction period is omitted; furthermore, it has been found that the more dilute the acid the more stable the solution during the time of the experiment; from this it follows that the velocity constant is greater.	Colloidal Pt (red) and colloidal Pt (black).	Sano: <i>Bull. Chem. Soc. Japan</i> , <b>14</b> , 121-131 (1939).



Table 14. Catalytic Oxidation of Amines.

Reaction	Catalyst	Observer
Oxidation of aniline with $\text{NaClO}_2$ to aniline black.	$\text{V}_2\text{O}_5$ , CuS.	
Oxidation of dimethyl aniline to Methyl Violet B.		Röhm and Haas A.-G. (Baker and Lauth) F.P. 71,970. (Refer to C. 1933 I 2608).
Oxidation of alicyclic amines with amino-groups in the side chains; yield with Cu, 54-57%; yield with Os, 30%; 1'-aminomethyl-cyclopropane is converted into the aldehyde of cyclopropane carbonic acid.	Cu or Os anhydride.	Schuilkin: <i>Zhur. Obshchei Khim.</i> 7 (69), 983-988 (1937); 7 (69), 989-993 (1937).
Oxidation of cyclohexylmethyl-amine and methods of preparation; cyclohexylcarbinol is passed with 3 parts by vol. $\text{NH}_3$ over the catalyst; T. 185°; 65% of the alcohol is converted, whereby three-fourths is present as primary amine; a 10% aqueous cyclohexylmethyl-amine emulsion is mixed with Cu powder; 21 $\text{O}_2$ are taken up per 3 g. of the amine and 46.4% hexahydrobenzaldehyde and small amounts of hexahydrobenzoic acid are formed.	Ni (the catalyst is prepared by boiling an alloy of 27% Ni and 73% Al with 1.5% NaOH); the action of ultraviolet light in the presence of catalyst Cu caused an increase in the yield up to 70%.	Lenarski: <i>Ibid.</i> , 9, 99-103 (1939).

Table 15. Catalytic Oxidation of Carbohydrates.

Reaction	Catalyst	Observer
Oxidation of sucrose with $\text{HNO}_3$ to oxalic acid; T. 160-170°.	$\text{V}_2\text{O}_5$ (0.1 g.).  40-65% $\text{HgNO}_3$ or $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .	Naumann, Moser and Lindenbaum: <i>J. prakt. Chem.</i> , 75, 148 (1907). Badische Anilin- und Soda Fabrik: Swiss P. 99,041. (Refer to C. 1923 IV 879K). E.P. 184,627 (1922).
Oxidation of mannose to tartaric acid.	$\text{V}_2\text{O}_5$ or $\text{HgSO}_4$ (2-5% of carbohydrate used).	Diamalt A.-G.: Aust. P. 89,263 (1922). Can. P. 233,734 (1923).
Oxidation of mannose.	Elements of the 5th, 6th and 8th groups of the Periodic System.	N. V. Industriale Mij V.h. (Noury and van der Lande): N.P. 57,462, Jan. 11, 1937.
Oxidation of cellulose with 50% $\text{H}_2\text{PO}_4$ to oxalic acid.	$\text{V}_2\text{O}_5$ .	Kolsky: U.S.P. 1,446,012 (1923).
Oxidation of cellulose with 70% $\text{H}_2\text{SO}_4$ to oxalic acid (1 mol. $\text{NO}$ : 15-20 mols $\text{O}_2$ ); T. 50°.	$\text{V}_2\text{O}_5$ .	Dr. Wacker Gesellschaft für die Elektrische Industrie: G.P. 409,948 (1925).
Oxidation of 900 g. glucose with 9 liters 90% $\text{H}_2\text{SO}_4$ and 3 liters 76% $\text{HNO}_3$ to oxalic acid; T. 50°; pressure 8 atm.; time 2 hours; 864 g. oxalic acid obtained, or 96% of the original substance.	$\text{V}_2\text{O}_5$ (30 g.).	Koepp Co.: G.P. 570,933, Kl 12o, Feb 20, 1933.

Table 16. Catalytic Oxidation of Ethers.

Reaction	Catalyst	Observer
Oxidation of dimethyl ether to $\text{CH}_3\text{O}$ ; T. 350°; yield, quantitative.	Cu or Ag.	Farbenfabrik vorm Meister Lucius Bräunig: G.P. 413,448 (1925).
Oxidation of ethyl ether to ethyl peroxide.	Active charcoal.	Demongin and Landon: <i>Bull. soc. chim.</i> (5), 2, 27 (1935).

Table 17. Catalytic Oxidation of Various Organic Compounds.

Reaction	Catalyst	Observer
Oxidation of organic cpds.	Ag powder.	Berthelot: <i>Bull. soc. chim.</i> (2), <b>34</b> , 135 (1880).
Oxidation of hydrocarbons to acetic acid.	Cu, pumice, asbestos.	Glock: G.P. 109,015 (1899).
Oxidation of hydrocarbons in the vapor phase to acetic acid.	Light metals.	Farbenfabriken vorm. Friederich Bayer & Co.: G.P. 346,520 (1917).
Oxidation of organic cpds.	Fe, Ni or Co chemically combined or in solid solution.	Badische Anilin- und Soda Fabrik: E.P. 254,460, Aug. 5, 1926. F.P. 593,942, Sept. 2, 1925.
Oxidation of organic cpds. in vapor phase.	V, Mo oxides; cpds. of the alkalies and alkaline earths not readily reducible are used as stabilizers.	Selden Co. (Jaeger): F.P. 649,292, Dec. 20, 1928.
Oxidation of organic cpds. in vapor phase with O <sub>2</sub> -containing gases.	A base exchanger not containing Si + stabilizer.	Selden Co. (Jaeger): E.P. 295,270, Oct. 3, 1928. E.P. 315,854, Sept. 11, 1929.
Oxidation of organic cpds. with O <sub>2</sub> or H <sub>2</sub> O <sub>2</sub> .	Fe.	Wieland and Franke: <i>Ann.</i> , <b>464</b> , 101-226 (1929).
Oxidation of hydrocarbons with air.	NO.	Bith and Lucas: <i>Ind. Eng. Chem.</i> , <b>21</b> , 633 (1929).
Oxidation of hydrocarbons with air or O <sub>2</sub> .	Vanadium.	Adadurow and Boreskow: <i>Zhur. Priklad. Khim.</i> , <b>6</b> (20), (1933). Lubarsky: <i>Ibid.</i> , <b>6</b> (20), 847 (1933). Lubarsky: B.P. 331,535 (1930).
Oxidation of organic cpds. in vapor phase.	Oxides of rare earths.	Lowdermilk and Day: <i>J. Am. Chem. Soc.</i> , <b>52</b> , 535-545 (1930).
Oxidation of saturated aliphatic hydrocarbons: T. 325°F.; pressure, sufficient to prevent dissociation of O <sub>2</sub> -containing organic cpds. formed; from CH <sub>4</sub> and its gaseous homologs, alcohols: methanol, ethanol and propanol, also aldehydes: CH <sub>3</sub> CHO as well as ketones and carbonic acids may be obtained.		Naimen and Leggett: U.S.P. 1,878,170, Sept. 20, 1932.
Oxidation of organic cpds. in vapor phase; (1) T. 350° (2) T. 250°	(1) MgO, MoO <sub>3</sub> or WO <sub>3</sub> ; reaction velocity increases with temp.; faster with MgO than with MoO <sub>3</sub> ; (2) NiO; activity of catalyst increases during the process; it is believed that the catalyst uses up a definite amount of O <sub>2</sub> per unit time at a definite temp. provided complete oxidation of substance takes place independently of the kind of material oxidized.	Charlot: <i>Compt. rend.</i> , <b>196</b> , 1224-1226 (1933).
Oxidation of high molecular weight aliphatic cpds. in liquid phase with O <sub>2</sub> -containing gases.	Mixtures of oleates, naphthenates, palmitates, cinnamates, abietates of Li+Ce, Na+Hg, Ca+Ce, Al+Mn, Na+Cr, Na+Mn, Mg+V, K+Al+Mn, Na+Al+V; 0.5% of the catalyst, e.g., 40% Na+60% Al; especially recommended are alkali or Al salts of the above-mentioned acids.	I. G. Farbenindustrie A.-G.: E.P. 386,715, Feb. 16, 1933. G.P. 567,983, Kl 120, Jan. 12, 1933.
Oxidation of acetone by persulfates in a 0.45 N H <sub>2</sub> SO <sub>4</sub> solution (1) S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> + Ag <sup>+</sup> → 2SO <sub>4</sub> <sup>2-</sup> + Ag <sup>+</sup> (measurably, slow) (2) CH <sub>3</sub> COOCH <sub>3</sub> + 4Ag <sup>+</sup> + 3H <sub>2</sub> O → CH <sub>3</sub> COO <sup>-</sup> + 4Ag <sup>+</sup> + 9H <sup>+</sup> + CO <sub>2</sub> (fast) acetone reacts with S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> twice as fast as with Cr <sup>3+</sup> and 1/5 as fast as with NH <sub>4</sub> <sup>+</sup> .	Ag ions.	Bekier and Kijowski: <i>Roczniki Chem.</i> , <b>15</b> , 136-152 (1935).

Table 17 (Continued).

Reaction	Catalyst	Observer
Oxidation of organic cpds.	Fe(NO <sub>3</sub> ) <sub>3</sub> solution together with an excess of MgCO <sub>3</sub> and a small amount of chromate mixed; the oxides obtained are dried, ground and replaced by a solution of Na <sub>2</sub> SiO <sub>3</sub> ; then molded, dried at 725° and reduced at 550°; a mixture of Fe, difficultly reducible metal oxides and Na <sub>2</sub> SiO <sub>3</sub> is used as a binding agent.	Carbide & Carbon Chemicals Corporation; Can. P. 352,767, Sept. 3, 1935.
Oxidation of hydrocarbons with oxidation products of H <sub>2</sub> SO <sub>4</sub> and persulfuric acid, also H <sub>2</sub> O <sub>2</sub> or O <sub>3</sub> .	CeSO <sub>4</sub> .	Haltman and Powell Corporation; U.S.P. 1,992,309, Feb. 26, 1935.
Oxidation of hydrocarbons with less than 10% by volume of O <sub>2</sub> to CH <sub>3</sub> O, CH <sub>3</sub> CHO, C <sub>2</sub> H <sub>5</sub> O; T. 600–1000°F.; 200–900 lbs. per sq. in. pressure.	Al phosphate; CuO on pumice; ZnO or Ag <sub>2</sub> O with phosphoric acid or salts or oxides of metals of the 3rd group.	Empire Oil and Refining Co. (Walker); U.S.P. 2,007,116, July 2, 1935.
Oxidation of mercaptans with O <sub>2</sub> -containing gases, such as air; T. 80–150°; partial O <sub>2</sub> pressure not below 1/10 atm.	Cu, Pb, Fe, Cr, Ni, Mn, Ag, Pt, or the corresponding oxides.	N. V. de Bataafsche Petroleum Mij; P.P. 792,586, Jan. 6, 1936.
Oxidation of coal by spraying with 600 g. of catalyst mixture "A."	Mixture "A" consists of: 18.0 kg. K <sub>2</sub> SO <sub>4</sub> 10.0 kg. Na <sub>2</sub> SO <sub>4</sub> 10.0 kg. B(OH) <sub>3</sub> 12.0 kg. Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> 2.0 kg. Na <sub>2</sub> CO <sub>3</sub> 12.0 kg. FeSO <sub>4</sub> 12.0 kg. MgSO <sub>4</sub> 12.5 kg. MnSO <sub>4</sub> dissolved in 50 l. boiling H <sub>2</sub> O, evaporated to dryness, and the salt mixture dehydrated at 100–150°.	Touston; P.P. 814,008, June 14, 1937.
Oxidation of cystine with H <sub>2</sub> O <sub>2</sub> to cystinic acid, also NH <sub>3</sub> , SO <sub>2</sub> and CO <sub>2</sub> ; a monomolecular reaction.	Vanadic acid sol.; Na tungstate and NH <sub>4</sub> tungstate also catalyze the reaction, but impure Na vanadate does not.	Ghosh and Karr; <i>J. Indian Chem. Soc.</i> , <b>14</b> , 249–253 (1937).
Oxidation of CCl <sub>4</sub> with water to CHCl <sub>3</sub> ; T. 15–50°.	Finely divided Fe; as catalysts may be used Pb, Cu, Mg, Sb or Te metals or their compounds; likewise in a mixture with salts of NH <sub>3</sub> : NH <sub>4</sub> Br, NH <sub>4</sub> acetate or NH <sub>4</sub> oxalate.	Dow Chemical Co. (Coleman, Hadler and Zuckerman); U.S.P. 2,104,703, Jan. 4, 1938.
Oxidation reactions.	Platinized Ni-Cr and Ni-Cr-Pd (Ni-Cr wire, ribbon or plates are covered by an oxide layer by heating to 800° and then the platinizing tincture is prepared according to Kundt (to 1 g. Pt chloride dissolved in 3 cc. alcohol, 10 cc. saturated alcoholic boric acid solution and a mixture of turpentine oil and lavender oil (1 : 1) are added); after drying, it is heated again to 300°; usually platinizing is repeated 2 or 3 times; likewise Pd is brought upon the catalyst; finely divided Pt or Pd on the oxide layer is a very active catalyst; it may be used instead of platinized asbestos, quartz, Pt or Pd black or other Pt catalysts).	Gerschenowitsch and Kotelkow; <i>Zhur. Priklad. Khim.</i> , <b>11</b> , 253–256 (1938).
Oxidation of furfural to maleic acid: 1.3 cc./hr. furfural to 2.27 mol/hr. air; T. 320°; time, 3 sec.; yield, 25%, initial substance, if liquid, led through a stream of O <sub>2</sub> or O <sub>2</sub> -containing gas and converted into a fog, in which single particles become charged with O <sub>2</sub> ; initial sub-	Mixture of V and Mo oxides or Bi vanadate; V <sub>2</sub> O <sub>5</sub> catalyst on pumice.	Research Corporation (Milas and Walsh); U.S.P. 2,118,567, May 24, 1938.

Table 17 (Continued).

Reaction	Catalyst	Observer
stance, if solid, reduced to powder or granulated and led in dispersed form through $O_2$ (T. 20–25°); then brought in contact with the catalyst at suitable temp. for 1–6 sec.		
Oxidation of bornyl chloride to camphene; T. 150°, 200°, 250°, 300° and 350°; yield, 66%; best yield obtained at 150°; for 10 g. bornyl chloride, 110 l. air and 80 g. water used; with rising temp., more HCl is split off and less camphene formed.	$V_2O_5$ .	Rutowski, Lossew and Meschetschko: <i>Zhur. Priklad. Khim.</i> , 11, 311–315 (1938).
Preparation of phthalic acid anhydride by oxidation in vapor phase.	Naphthalene containing tar-forming ingredients.	National Aniline and Chemical Co., Inc. (Riegler); U.S.P. 2,149,362, March 7, 1939.
Oxidation of cyclohexane, cyclohexene, cyclohexanol, cyclohexanone, cyclopentane, cyclopentadiene, and adipinic acid; T. 320–470°; excess of air and contact time of few tenths of a second; in all cases as chief solid product maleic acid is obtained in yields from 14–32%; the formation of maleic acid with quinone as intermediate product as well as cyclohexene, adipinic acid and cyclopentanone is discussed; the observed $CH_2O$ formation is explained better by the second mechanism.	$V_2O_5$ on pumice.	Milas and Walsh: <i>J. Am. Chem. Soc.</i> , 61, 633–35 (1939).
Oxidation and decomposition of saturated cyclic ketones; cyclohexanone gives aldehyde of adipinic acid and cyclopentanone gives aldehyde of glutaric acid; in the case of cyclohexanone as side reaction the oxidation of the $CH_2$ group is observed, which corresponds to the course of the biochemical oxidation; thereby oxycompounds are formed, while the reaction here leads to 1,4-cyclohexandion; if the carbonyl lies beside a $CH_2$ group and also a $CH$ group of a side chain, a break in the ring between the carbonyl and the C atom which is poorer in hydrogen takes place; from menthone, $\beta$ -methyl-isobutyryl- $\alpha$ -valeric acid is formed, and from tetrahydrocarvone, $\beta$ -isopropylacetyl- $\alpha$ -valeric acid.	Pervanadic acid (the catalyst is obtained by pouring over $V_2O_5$ a 30% $H_2O_2$ ; brown-yellow to green, soluble in water, alcohol, acetone in the presence of $H_2O_2$ ).	Treibs: <i>Ber.</i> , 72, 1194–99 (1939); refer also to Giarnician and Silber: <i>Ber.</i> , 46, 3077 (1913).

Table 18. Catalytic Oxidation of Various Oils.

Reaction	Catalyst	Observer
Oxidation of fatty oils; T. 80–90°; pressure 20 atm.	0.1% Co borate, 3½ hrs. 0.2% Mn borate, 4 hrs. Ni and Fe salts.	Rai: <i>J. Soc. Chem. Ind.</i> , 36, 948 (1917).
Oxidation of China wood oil.	Co compounds. Mn and Pb cpds. used in amounts of 0.03%–0.26%.	Rhodes and Ling: <i>Ind. Eng. Chem.</i> , 17, 508 (1925). Ludwig: <i>Ibid.</i> , 17, 1160 (1925).
Oxidation of solar oils to fatty acids in two stages: (1) formation of aldehydes. (2) formation of fatty acids (industrial process).	Oxides of difficultly reducible electro-negative metals of an atomic weight greater than 40 but with a small atomic volume: Ti, V, Cr, Mn, Zr, Nb, Mo, Ta, W and U, or acid salts of these; Fe, Cu, Ni, La, Zn, Co, Th, or rare earths.	James: U.S.P. 1,759,620 (1930). Krauch: Proc. Intern. Conf. Bituminous Coal, 2nd Conf., 1928.

Table 18 (Continued).

Reaction	Catalyst	Observer
Oxidation of heavy oils with water vapor to combustible gases.	AlCl <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , NiO, Pd, Pt, Cu. Fe in a colloidal state and may be applied: (1) directly; (2) by means of a dispersion agent, such as ether, alcohol, CH <sub>4</sub> , petroleum; (3) by adding the dispersion agent dropwise; (4) by adding the catalyst to the evaporating water, or directly to the water vapor in the motor; conversion of the catalyst into the colloidal state occurs: (1) by dispersing in small particles in water before evaporating; (2) by applying oscillatory electric discharge; (3) by subjecting to the action of an electric arc light.	Zube, Möller and Starnad: Austrian P. 148, 333, Jan. 11, 1937.
Oxidation of oils subjected to the action of N <sub>2</sub> O <sub>4</sub> .	Fe <sub>2</sub> O <sub>3</sub> ; ferri-ricinoleate added in amounts 0.05-5%.	Egerton: E.P. 497,973, Jan. 23, 1939.
Oxidation of turbine oil.	Cu (inhibitors are active if they are insoluble in water).	Farmer, H.: <i>Elec. World</i> , 111, (N. 20), 36-37, 103 (1939).
Oxidation of mineral transformer oil; it is subjected in a steel bomb to an O <sub>2</sub> pressure of 250 lbs. per sq. in. at 140° for 24 hrs.; this is a method for testing the chemical stability of mineral transformer oils; it is said to be superior to the Baader and Snyder test.	Cu.	Clark: <i>Proc. Am. Soc. Testing Materials</i> , 38, 507-19 (1938).

Table 19. Catalytic Oxidation of Benzene.

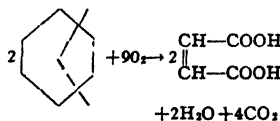
Reaction	Catalyst	Observer
Oxidation of trichloro-benzene to benzoic acid.	Fe powder; ZnCl <sub>2</sub> .	Schultze: G.P. 82,927, Kl 12, June 12, 1894. G.P. 85,493, Kl 12, Sept. 10, 1895. Mathieson: U.S.P. 1,557,153 (1924).
$C_6H_5 \cdot CCl_3 + 2H_2O \rightarrow C_6H_5 \cdot COOH + 3HCl$		Bayer: G.P. 98,706 (1897). Küchler and Buff: G.P. 126,421 (1900). Boehringer: G.P. 281,212 (1913). Gelsenkirchner Bergwerke A.-G.: G.P. 403,489 (1921).
Oxidation of benzene with CO to benzaldehyde in the presence of CuCl <sub>2</sub> and HCl.	AlCl <sub>3</sub> .	
Oxidation of benzene with O <sub>2</sub> to maleic acid (industrial process).	V <sub>2</sub> O <sub>5</sub> .	Barrett Co.: G.P. 365,894 (1920). U.S.P. 1,377,534 (1920). Boehringer: G.P. 478,726 (1927).
Oxidation of benzene with O <sub>2</sub> to maleic acid; T. 400-450°.	V <sub>2</sub> O <sub>5</sub> .	Barrett Co.: U.S.P. 1,380,277 (1921). U.S.P. 1,515,299 (1924). F.P. 526,005 (1921). F.P. 535,086 (1922).
 $2 \text{ (benzene ring) } + 90^\circ \rightarrow 2 \begin{array}{l} \text{CH-COOH} \\ \text{CH-COOH} \end{array} + 2H_2O + 4CO_2$		
Oxidation of benzene.	Vanadyl zeolite.	Monsanto Chemical Works:
Oxidation of benzene.	V <sub>2</sub> O <sub>5</sub> , melted and pulverized.	Selden Co. (Jaeger): Swed. P. 57,335 (Refer to C. 1925 II 1621).
Oxidation of benzene to phenol by heating with a 20% NaOH solution in an autoclave for about 1 hr.; T. 300-360°.	Oxides of U and V.	Dow Chemical Co.: U.S.P. 1,547,725 (1925).
Oxidation of benzene to phenol.	Oxides of U and V.	Dow Chemical Co.: U.S.P. 1,595,299 (1926).

Table 19 (Continued).

Reaction	Catalyst	Observer
Oxidation of benzene to maleic or fumaric acid, and cresol to salicylic acid.	Non-reducible oxides or their salts: sulfates, phosphates, halides, arsenates, borates, carbonates and bismuth cpds. of alkalies or alkaline earths.	Selden Co. (Jaeger): E.P. 291,419, Jan. 24, 1929.
Oxidation of benzene with water vapor to phenol; T. 700°.	Silicic acid gel.	Federal Phosphorus Co. (Kennedy and Lloyd): U.S.P. 1,735,327 (1929).
✓ Oxidation of benzene in vapor phase with 1-5% O <sub>2</sub> to phenol; T. 400-500°; yield, 75%.	Oxides of Cr, Mo, W, U, V, Nb or Ta.	I. G. Farbenindustrie A.-G.: G.P. 501,467 (1929).
✓ Oxidation of benzene with a gas containing 1-5% O <sub>2</sub> (air diluted with N, CO <sub>2</sub> or water vapor) to phenol; T. 400-500°; yield, 75%.	Oxides of Cr, Mo, W, U, V, N or Ta.	I. G. Farbenindustrie A.-G.: G.P. 501,467 (1930).
Oxidation of benzene in vapor phase to maleic acid.	Active silicate or other non-exchanging bases containing oxides of Fe, Co, Ni, Cu or Al.	Selden Co. (Jaeger): U.S.P. 1,811,363, Mar. 29, 1932.
Oxidation of benzene to maleic acid.	Alkali carbonates or bicarbonates with small amounts of mineral substances.	Carpentier: <i>Union pharm.</i> , 92, 65-69 (1932).
Oxidation of benzene with O <sub>2</sub> to maleic acid (benzene-air mixture preheated up to 360°); T. 410-430°; yield 14-17%; main reaction:	V <sub>2</sub> O <sub>5</sub> on pumice or asbestos fibers.	Salkind and Solotarew: <i>Zhur. Priklad. Khim.</i> , 6, 681-684 (1933).
$2C_6H_6 + O_2 \rightarrow 2C_6H_5OH \rightarrow$ $O = \text{C}_6\text{H}_4 = O + 3O_2 \rightarrow$ $HOOC \cdot CH = CH \cdot COOH + 2CO_2$ <p>Benzoquinone is formed as a side product, the amount of which increases with increase in fatigue of the catalyst; side reaction:</p> $C_6H_4O_2 + 2O_2 \rightarrow \begin{array}{c} CH-CO \\    \quad \diagup \\ CH-CO \end{array} O +$ $H \cdot CHO + CO_2$		
Oxidation of 50 g. trichlorobenzene with 125 cc. O <sub>2</sub> to acetophenone; T. 130°; yield: 15.8 g. acetophenone 1.24 g. benzoic acid 3.1 g. phenylmethyl carbinol; time, 45 min.	MnO <sub>2</sub> (0.5 g.).	Senseman and Strubbs: <i>Ind. Eng. Chem.</i> , 25, 1286-1287 (1933).
Oxidation of benzene in vapor phase with air or O <sub>2</sub> to maleic acid, quinone and H <sub>2</sub> O; T. 370° and 450°; max. yield maleic acid 38%.	V <sub>2</sub> O <sub>5</sub> .	Pigulewski and Yarschemskaja-Kornilowa: <i>Zhur. Obshchei Khim.</i> , 5, (67), 1620-1628 (1935).
Oxidation of benzene to maleic acid; ratio benzene to air = 1/50 to 1/60; T. 450°; yield, up to 57% of the total benzene; twice through yields 84.5%; productivity of catalyst reaches 200 g./l./hr.	Mixture of V <sub>2</sub> O <sub>5</sub> (70%) + MoO <sub>3</sub> (30%) with addition of Co <sub>2</sub> O <sub>3</sub> (5%).	Kiprianow and Sehosstan: <i>Zhur. Priklad. Khim.</i> , 11, 471-480 (1938).
Oxidation of benzene to maleic acid in a good yield.	Vanadic acid (I) forming with trimethyl- or tetramethylbenzyl ammonium hydroxide (II) extremely water-soluble salts which in solution are viscous, sticky, and adhere well to inert carriers (pumice, graphite, silica gel, activated and granulated Al); by heating to 350-450° in air stream, V <sub>2</sub> O <sub>5</sub> (III) is obtained, yellow to orange-brown; 1.5 kg. ammonium	Röhm and Haas Co. (Andrews): U.S.P. 2,134,543, Oct. 25, 1938.

Table 19 (Continued).

Reaction	Catalyst	Observer
	metavanadate is dissolved in 5.3 l. 38.6% aqueous solution of II by mild heating and then 15 g. "filtros" (porous silica gel, grain size 12-20 meshes) added and with stirring heated to decomposition, passed through a 28-mesh sieve and heated in air stream to 400° until catalyst shows orange-brown; contains about 0.8 kg. (III).	

Table 20. Catalytic Oxidation of Toluene.

Reaction	Catalyst	Observer
Oxidation of toluene to benzaldehyde and benzoic acid.	Charcoal, brown coal.	I. G. Farbenindustrie A.-G.: G.P. 203,848 (1899).
Oxidation of toluene to benzaldehyde and benzoic acid.	MnO <sub>2</sub> , chromic acid.	Badische Anilin- und Soda Fabrik: P.P. 276,258 Raschig G.m.b.H.: <i>Chem. Ztg.</i> , 24, 446 (1900).
Oxidation of toluene in vapor phase with air.	V <sub>2</sub> O <sub>5</sub> , MoO <sub>3</sub> , bases.	Wohl: G.P. 347,610 (1916). E.P. 156,244 (1921).
Oxidation of toluene in liquid phase with 35% HNO <sub>3</sub> to benzoic acid; yield, 70-80%.	MnO <sub>2</sub> .	Seydel Chemical Co.: U.S.P. 1,576,999, March 16, 1926.
Oxidation of toluene in liquid phase to benzoic acid.	KMnO <sub>4</sub> .	Chemische Werke Grenzach: G.P. 377,990 (1915).
Oxidation of toluene in the vapor phase with air.	V <sub>2</sub> O <sub>5</sub> , MoO <sub>3</sub> , bases.	Barrett Co.: U.S.P. 1,377,534 (1920). Fischer: G.P. 364,442 (1919).
Oxidation of toluene to benzaldehyde and benzoic acid.	H <sub>3</sub> PO <sub>4</sub> on pumice.	Badische Anilin- und Soda Fabrik: G.P. 408,184 (1920).
Oxidation of toluene in vapor phase to benzaldehyde and benzoic acid.	ZnO + Cr <sub>2</sub> O <sub>3</sub> .	Badische Anilin- und Soda Fabrik: G.P. 415,686 (1923).
Oxidation of toluene to benzaldehyde and benzoic acid.	V <sub>2</sub> O <sub>5</sub> .	Scalione and Frazer: E.P. 166,285, Aug. 11, 1921.
Oxidation of toluene to benzaldehyde and benzoic acid; yield, 75-80%.	Na dichromate with kieselguhr.	Eichwald and Hardt: G.P. 360,528 (1922).
Oxidation of toluene to benzaldehyde and benzoic acid.	H <sub>2</sub> O.	Eckart: E.P. 182,487 (1922). F.P. 553,262 (1923).
Oxidation of toluene with air or CO <sub>2</sub> .	V <sub>2</sub> O <sub>5</sub> .	I. G. Farbenindustrie A.-G.: G.P. 408,184 (1925).
Oxidation of toluene with air to benzaldehyde and benzoic acid (preheated up to 60-70°; T. 400°; aldehyde and acid separated on cooling; continuous process.	Cu molybdate and U.	I. G. Farbenindustrie A.-G.: G.P. 446,912 (1927).
Oxidation of toluene in vapor phase to benzaldehyde and benzoic acid; T. 340-380°.	Oxides of V, Mo, Ta, W, Cr, U, Mn, Bi, Fe, Co, Ni, Cu, Ag, or mixtures, together with zeolites; Al double silicates or simple Al silicates, natural zeolites, or feldspar.	Selden Co. (Jaeger): U.S.P. 1,694,122, Dec. 4, 1928.
Oxidation of toluene to benzaldehyde and benzoic acid.	Sn, Bi, Co, Pb vanadates.	Marted and Coke: E.P. 237,688, Aug. 21, 1925. Marted and Dunsby: <i>J. Chem. Soc.</i> , 1928, 1439-1442.
Oxidation of toluene in vapor phase.	Contact mass.	Gas, Light and Coke Co. (Adam, Sherman and Cuckner): E.P. 331,535, July 31, 1930.

Table 20 (Continued).

Reaction	Catalyst	Observer
Oxidation of toluene with 10 parts water; T. 235–240°; pressure 60 atm.	Fe hydroxide (3–4%), FeO(OH).	F.P. 676,826 (1930). (Refer to C. 1930 I 3831).
Oxidation of toluene with air to benzaldehyde and benzoic acid; T. 400°.	Active silicic acid.	I. G. Farbenindustrie A.-G. (Mittasch and Luther); G.P. 520,828, Kl 12o, March 31, 1931.
Oxidation of toluene to benzaldehyde and benzoic acid.	V and Mo acids on silica gel.	Gewerkschaft Mathias Stinnes; G.P. 553,408 (1931).
Oxidation of toluene.	Heavy metal oxides with granular kieselguhr as carrier.	Selden Co. (Jaeger); U.S.P. 1,935,054 (1933).
Oxidation of toluene in vapor phase to benzaldehyde and benzoic acid; T. 300°; pressure 12 mm. Hg.	MgO, MoO <sub>3</sub> , WO <sub>3</sub> .	Charlot: <i>Compt. rend.</i> , 196, 1224–1226 (1933).
Oxidation of toluene in vapor phase.	Higher oxides of Mo or V reduced in an acid solution with metals, e.g., Fe-Cr together with non-reducible oxides applied on a carrier.	Bogdanow; Russ. P. 38,633, Sept. 30, 1934.
Oxidation of toluene.		Selden Co. (Jaeger); U.S.P. 1,942,817, Jan. 9, 1934.
Oxidation of toluene with air to benzaldehyde and benzoic acid; T. 280–450°.	V <sub>2</sub> O <sub>5</sub> or Sn vanadate with a small amount of silica gel.	Chowhury and Choudhury: <i>J. Indian Chem. Soc.</i> , 11, 185 (1934).
Oxidation of toluene to benzaldehyde and benzoic acid.	Al <sub>2</sub> O <sub>3</sub> , MoO <sub>3</sub> and ThO <sub>2</sub> (mixed catalyst).	American Cyanamid and Chemical Corporation and Heyden Chemical Corporation (Reynolds); U.S.P. 2,042,632 (1936).
Oxidation of toluene in vapor phase with air; ratio 38 : 1; T. 390–650°; at 575° 20% toluene converted into benzaldehyde.	Uranyl molybdate and boron carbide on a granulated Al.	Parks and Katz: <i>Ind. Eng. Chem.</i> , 28, 319–323 (1936).
Oxidation of toluene to benzaldehyde only; T. 600°.	Metal oxides of the 5th and 6th groups on Al <sub>2</sub> O <sub>3</sub> .	Parks and Katz: <i>Ind. Eng. Chem.</i> , 28, 319–323 (1936).
Oxidation of aromatic hydrocarbons in liquid phase, e.g., methyl-substituted benzene, as well as toluene, is oxidized to the corresponding acid, especially benzoic acid, with a basic inorganic substance in aqueous solution, especially alkali, such as NaOH in O <sub>2</sub> -containing gas, e.g., air.	Alkali chromate or bichromate; Cr maintains its catalytically active state.	Mares; U.S.P. 2,120,672, June 14, 1938.
✓ Oxidation of toluene; T. 300–700°.	Mo oxide and U oxide.	Barrett Co. (Craven); U.S.P. 1,636,854, July 26, 1927.
Oxidation of toluene, its derivatives and homologs; homologs of benzene and their derivatives; partial oxidation is of the same order of magnitude in all cases for a given catalyst though somewhat increased for substances with highly branched side chains.	SnO <sub>2</sub> , Cr <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> , WO <sub>3</sub> , CoO; the majority of the catalysts determine the amount of partial oxidation products formed and the extent of total oxidation to CO <sub>2</sub> and H <sub>2</sub> O; for a given catalyst complete oxidation, as defined by the volume of CO <sub>2</sub> formed in a given time at a definite temp., is constant and independent for certain limits of the substance oxidized and of the conc. of the substances and the volume of gas produced; the ratio of partial to total oxidation is more characteristic of the catalyst than of the compound oxidized.	Charlot: <i>Bull. soc. chim.</i> , 53, 52–57 (1933); <i>Chem. Abs.</i> , 26, 2714; 27, 5304; <i>Compt. rend.</i> , 194, 374–76 (1932); <i>Bull. soc. chim.</i> , 53, 577–81 (1933).



Table 21. Catalytic Oxidation of Benzaldehyde.

Reaction	Catalyst	Observer
Oxidation of benzaldehyde to benzoic acid.	NiO, Co <sub>2</sub> O <sub>3</sub> , CuO.	Blanc: F.P. 586,383 (1925). Keiff: <i>J. Am. Chem. Soc.</i> , <b>48</b> , 2893-2899 (1926).
Oxidation of benzaldehyde with O <sub>2</sub> ; effect of varying conc., time, temp. and solvents upon benzaldehyde were studied and active molecules and chain reactions considered in the mechanism of the reaction.	Ozone (catalytic action arises from the extra energy available when O <sub>3</sub> replaces O <sub>2</sub> for auto-oxidation).	Briner, Demolis and Paillard: <i>J. Chem. Phys.</i> , <b>29</b> , 339-361 (1932). Briner, Demolis and Paillard: <i>Helv. Chim. Acta</i> , ( ). (Refer to C. 1931 II 2559).
Oxidation of benzaldehyde with Na <sub>2</sub> SO <sub>3</sub> in the absence of O <sub>2</sub> at a low temp.	Ozone (the action of O <sub>3</sub> is greater in pure O <sub>2</sub> than in O <sub>2</sub> -N <sub>2</sub> mixtures).	Briner, Demolis and Paillard: <i>Helv. Chim. Acta</i> , ( ). (Refer to C. 1932 I 1872). (Refer to C. 1933 I 179.)
Oxidation of hydrocarbons in vapor phase as a source of industrially valuable products; reaction product consists of unsaturated hydrocarbons with 1 and 2 double bonds, aromatic hydrocarbons, saturated and unsaturated aliphatic aldehydes, saturated and unsaturated ketones, lactones, alcohols, small amounts of carbonic acids and phenols.		Piotrowski and Winkler: <i>Neft</i> , <b>34</b> (No. 16), 1-3, April 20, 1938.

Table 22. Catalytic Oxidation of Naphthalene.

Reaction	Catalyst	Observer
Oxidation of naphthalene to phthalic acid anhydride.	Hg in strong H <sub>2</sub> SO <sub>4</sub> solution.	Badische Anilin- und Soda Fabrik (Sapper); G.P. 91,202 (1896).
Oxidation of naphthalene in vapor phase to phthalic acid anhydride.	V <sub>2</sub> O <sub>5</sub> , MoO <sub>3</sub> .	Wohl: G.P. 347,610 (1916). B.P. 119,517 (1917). Barrett: U.S.P. 1,489,741 (1922).
✓ Oxidation of naphthalene to phthalic acid anhydride; T. 350-450°.	MoO <sub>3</sub> .	Selden Co. (Jaeger): Swiss P. 87,967 (1919). Swed. P. 54,880 (Refer to C. 1924 I 1714).
Oxidation of naphthalene to phthalic acid anhydride; T. 300°.	VOCl <sub>3</sub> .	British Dyestuffs Corporation: E.P. 164,785 (1920).
Oxidation of naphthalene to phthalic acid anhydride; T. 330°.	V <sub>2</sub> O <sub>5</sub> on pumice.	Wohl: Swiss P. 88,189 (1920). Swiss P. 95,507 (1922).
Oxidation of naphthalene to phthalic acid anhydride; T. 450°.	TiO <sub>2</sub> on pumice.	Attack and British Alizarina Co.: E.P. 182,843 (1922).
Oxidation of naphthalene to phthalic acid anhydride; T. 450°.	Al <sub>2</sub> O <sub>3</sub> on powdered pumice.	Barrett Co. (Downs): U.S.P. 1,374,722 (1921).
Oxidation of naphthalene to phthalic acid anhydride.	Vanadic acid on bone charcoal and kieselguhr.	Orloff: G.P. 347,610 (1922). G.P. 379,822 (1925).
✓ Oxidation of naphthalene to phthalic acid anhydride; T. 450°.	Al <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> , MoO <sub>3</sub> .	Barrett Co.: U.S.P. 1,489,741 (1924).
Oxidation of naphthalene to phthalic acid anhydride; T. 260-310°.	W vanadate.	Maxted: E.P. 228,771 (1924). G.P. 379,822 (1923).
Oxidation of naphthalene to phthalic acid anhydride; T. when heated with air, 100-110°; heated over catalyst, 300-500°; a large amount of air used for adsorbing heat separated in the reaction.	V <sub>2</sub> O <sub>5</sub> or MoO <sub>3</sub> .	Dupont: U.S.P. 1,515,299 (1924). U.S.P. 1,599,228 (1926).
Oxidation of naphthalene to phthalic acid anhydride.	Sn or Bi vanadate.	Maxted and Coke: E.P. 228,771, March 5, 1925.

Table 22 (Continued).

Reaction	Catalyst	Observer
Oxidation of naphthalene to phthalic acid anhydride.	Bi (better catalyst than Hg).	Menke: <i>Rec. trav. chim.</i> , <b>47</b> , 668-672 (1928).
Oxidation of naphthalene to phthalic acid anhydride or naphthoquinone, depending on the catalyst and the reaction temp.	Catalysts containing artificial zeolites 42 parts $K_2SiO_3$ 70 parts zeolite 18 parts $V_2O_5$ dissolved in concentrated KOH to which is added 5 parts $Al_2O_3$ in KOH or NaOH, heated to 60°, 10% $H_2SO_4$ added until viscous, filtered, precipitate dried at temp. not exceeding 100°, and powdered.	Selden Co. (Jaeger): E.P. 296,075 (1928). F.P. 649,292 (1929). U.S.P. 1,515,299 (1925). U.S.P. 1,692,126 (1928). U.S.P. 1,850,797 (1932).
Oxidation of naphthalene to phthalic acid anhydride.	V metal + oxides of Mo, W, Cr, U which prevent formation of lower oxides of V.	Tokishige Kusama: <i>Bull. Chem. Soc. Japan</i> , 1752 (1929).
Oxidation of naphthalene to phthalic acid anhydride; T. 400-450°. (1) yield, 7%. (2) yield, 62%.	Vanadic acid impregnated in silica gel either by: (1) precipitating or (2) melting.	Gewerkschaft Mathias Stinnes: G.P. 553,408 (1931).
Oxidation of naphthalene with air, ratio 1 : 20, to phthalic acid anhydride; T. 360-420°.	$Al_2O_3$ on carbides of elements of the 4th group.	Selden Co. (Jaeger): U.S.P. 1,930,716 (1933).
Oxidation of naphthalene to phthalic acid anhydride.	Vanadic acid on melted $Al_2O_3$ carrier.	Dupont: U.S.P. 2,034,896 (1936).
Oxidation of naphthalene to phthalic acid anhydride, using gas containing $O_2$ in the molecular ratio: 1 : 330-1 : 400; T. 450-600°.	Oxidation accelerator.	Solvay Process Co. (Rogers and Porter): U.S.P. 2,071,361, Feb. 23, 1937.
Oxidation of naphthalene to phthalic acid anhydride.	Heat exchange agent—diphenyl.	Reynolds: U.S.P. 2,081,120, May 18, 1937.
Oxidation of naphthalene with $O_2$ to maleic acid.	$ZnO$ , $CdO$ and $Al_2O_3$ .	
Oxidation of naphthalene to phthalic acid anhydride with $O_2$ -containing gases.	Metals of the 5th and 6th groups of the Periodic System such as V; the container is coated with Ni or Al, or the catalyst is supported by these metals.	American Cyanamid and Chemical Corporation (Andrews): U.S.P. 2,120,538, June 14, 1938.

Table 23. Catalytic Oxidation of Tetralin.

Reaction	Catalyst	Observer
Oxidation of Tetralin with oxygen to Tetralin peroxide; T. 60°.	Mn, Co and Pb oleate.	Yamada: <i>J. Soc. Chem. Ind. Japan</i> , <b>40</b> , 422B-424B (1937).

Table 24. Catalytic Oxidation of Acenaphthene.

Reaction	Catalyst	Observer
Oxidation of acenaphthene to acenaphthene quinone; T. 400°.	$V_2O_5$ or other oxides of the 5th and 6th groups on pumice.	I. G. Farbenindustrie A.-G.: G.P. 428,088 (1926). G.P. 441,163 (1927). Barrett Co.: U.S.P. 1,439,500 (1922).
Oxidation of acenaphthene with water vapor at high temp.	Alkali or alkaline-earth metal + catalyst of the reduction, hydrogenation or dehydrogenation group; a metal of the 5th or 6th group with V in a non-exchangeable form.	Selden Co. (Jaeger): U.S.P. 1,844,392, Feb. 9, 1932.
Oxidation of acenaphthene in solution with $O_2$ ; T. not greater than 310° (at high temp., acenaphthene readily auto-oxidizes); pressure, 8-60 kg./sq.cm.; (to prevent carbonization of acenaphthene the solvent o-dichlorobenzene is used).	$MnNO_3$ (best catalyst, $CuHNO_3$ and oxides).	Paillard and Duckert: <i>Helv. Chim. Acta</i> , <b>16</b> , 773-783 (1933).

Table 24 (Continued).

Reaction	Catalyst	Observer
Oxidation of acenaphthene with air, ratio 1 : 40, to naphthalic anhydride; T. 380–420°.	Alkalies or Al cpds. made into a paste with kieselguhr and water on which is precipitated Ag vanadate; Ag vanadate: kieselguhr, 1 : 4 to 1 : 6; catalyst stabilized by adding 3–5% Na <sub>2</sub> CO <sub>3</sub> or K <sub>2</sub> CO <sub>3</sub> before impregnating with vanadate solution.	Selden Co. (Jaeger); U.S.P. 1,935,054 (1933).

Table 25. Catalytic Oxidation of Anthracene.

Reaction	Catalyst	Observer
Oxidation of anthracene to anthraquinone.	V <sub>2</sub> O <sub>5</sub> , MoO <sub>3</sub> .	Wohl: G.P. 347,610 (1916). Conover and Gibbs: U.S.P. 1,417,367 (1917). Barrett Co. (Weiss and Downs): U.S.P. 1,355,098 (1918).
Oxidation of anthracene to anthraquinone.	H <sub>2</sub> VO <sub>4</sub> on pumice.	Badische Anilin- und Soda Fabrik: G.P. 408,184 (1920).
Oxidation of anthracene to anthraquinone.	V <sub>2</sub> O <sub>5</sub> , MoO <sub>3</sub> .	Selden Co. (Jaeger): E.P. 173,723 (1920).
Oxidation of anthracene with O <sub>2</sub> to anthraquinone; T. 100–120°; under pressure; for higher temp.*	Cu or Ag vanadate, V <sub>2</sub> O <sub>5</sub> or Cu acetate.*	Wohl: G.P. 388,382 (1923). G.P. 349,089 (1922). E.P. 156,244 (1920).
Oxidation of anthracene with air to anthraquinone.	Al <sub>2</sub> O <sub>3</sub> .	Dennstedt and Hassler: G.P. 203,848 (1923).
Oxidation of anthracene to anthraquinone; T. 425° (opt.); yield, 81.2%.	V <sub>2</sub> O <sub>5</sub> .	Sensemann and Nelson: <i>Ind. Eng. Chem.</i> , 15, 521 (1923).
Oxidation of anthracene with air to anthraquinone; T. 400–430°; yield 40–50%.	Boric acid on ton pieces or melted boric acid on silica gel or kieselguhr.	Badische Anilin- und Soda Fabrik (Mittasch, Willfroth and Balz): G.P. 397,212 (1924).
Oxidation of anthracene with carbonic acid.		I. G. Farbenindustrie A.-G.: G.P. 408,184 (1924).
Oxidation of anthracene to anthraquinone.	Minerals or rare earths containing didymium.	Field and Owen: E.P. 265,672, March 10, 1927.
Oxidation of anthracene to anthraquinone; T. 300–500°.	V <sub>2</sub> O <sub>5</sub> , MoO <sub>3</sub> , UO <sub>3</sub> .	Bruckner: "Katalytische Reaktionen in der organischen chemischen Industrie," Teil I, p. 112–114, 1930.
Oxidation of anthracene with air to anthraquinone; T. 360–450°.	Base-exchanging contact masses; 25% kieselguhr + silicates + potassium vanadate (vanadic acid in the presence of H <sub>2</sub> SO <sub>4</sub> converted into blue vanadyl sulfate and to it is added 0.1N KOH to obtain potassium vanadate); MnSO <sub>4</sub> may be added and the whole converted into a gel.	Selden Co. (Jaeger): U.S.P. 1,880,322 (1932).
Oxidation of anthracene in vapor phase to anthraquinone; T. 400°.	A mixture containing at least one zeolite (reaction product of at least one silicate and one metal salt such as K vanadate and at least one salt of Cu or Ni).	Selden Co. (Jaeger): U.S.P. 1,886,023, Jan. 11, 1932. Selden Co. (Jaeger and Bertsch): U.S.P. 1,840,450, Jan. 12, 1932.
Oxidation of anthracene or its derivatives to 2-aminoanthraquinone; T. 180–185°; yield, 94%.	Cu <sub>2</sub> O, NH <sub>4</sub> NO <sub>3</sub> , KClO <sub>3</sub> ; 28–40% aqueous NH <sub>3</sub> .	Groggins: U.S.P. 1,892,302, Dec. 27, 1932.
Oxidation of anthracene with air to anthraquinone.	Al <sub>2</sub> O <sub>3</sub> on carbides of the 4th group.	Selden Co. (Jaeger): U.S.P. 1,930,716 (1933).
Oxidation of anthracene to anthraquinone.	Granular diatomite used as carrier for oxidation catalysts such as heavy metal oxides.	Selden Co. (Jaeger): U.S.P. 1,935,054 (1933).
Oxidation of anthracene to anthraquinone; T. 200–280°.	Fe or Ag salts of vanadic acid or finely dispersed vanadic acid obtained from NH <sub>4</sub> vanadate, vanadium chloride or oxychloride or vanadic esters.	Shindlin: G.P. 578,723, Kl 12o, June 16, 1933.

Table 25 (Continued).

Reaction	Catalyst	Observer
Oxidation of anthracene to anthraquinone with chlorates in a weak $\text{H}_2\text{SO}_4$ solution which may be replaced by sodium dichromate in $\text{H}_2\text{SO}_4$ .	$\text{V}_2\text{O}_5$ .	Underwood, Jr. and Walsh; <i>J. Am. Chem. Soc.</i> , <b>58</b> , 646-647 (1936).
Oxidation of anthracene or its derivatives with air, $\text{O}_2$ , $\text{O}_3$ , or CO gas; T. not over $400^\circ$ ; pressure, 10-100 atm.		Chebotar and Wallach: U.S.P. 2,084,382, June 22, 1937

Table 26. Catalytic Oxidation of Phenanthrene.

Reaction	Catalyst	Observer
Oxidation of phenanthrene to phthalic anhydride and maleic acid.	$\text{Al}_2\text{O}_3$ precipitated on carbides of elements of the 4th group of the Periodic System.	Selden Co. (Jaeger): U.S.P. 1,930,716 (1933).
Oxidation of phenanthrene with air to phthalic acid; T. $370^\circ$ ; 4 sec. contact time; yield, 22% (air saturated with $\text{H}_2\text{O}$ at room temp.; addition of $\text{H}_2\text{O}$ unfavorable to a good yield) yield, 30% yield, 41%	$\text{V}_2\text{O}_5$ on pumice or mixed catalysts of V with Mo, U, or W. 25% $\text{NH}_4\text{VO}_3$ on pumice.  10% Mo + 90% V. 30% U + 70% V.	Salkind and Kessarew: <i>Zhur. Priklad. Khim.</i> , <b>10</b> , 99-104 (1937).

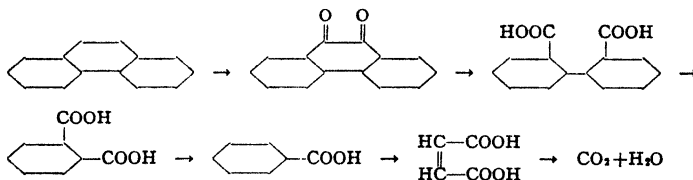


Table 27. Catalytic Oxidation of Various Aromatic Compounds.

Reaction	Catalyst	Observer
Oxidation of anthraquinone to hydroxylated derivatives.	Boric acid. Boric acid + $\text{HgO}$ .  Hg in fuming $\text{H}_2\text{SO}_4$ . $\text{SeO}_2$ in conc. $\text{H}_2\text{SO}_4$ .	Bayer (Schmidt): G.P. 81,481 (1893). G.P. 81,961 (1893). G.P. 162,035 (1904). Badische Anilin- und Soda Fabrik: G.P. 153,129 (1903). G.P. 162,035 (1904).
Oxidation of pyrogallol with $\text{H}_2\text{O}_2$ .	Fe greater than Cu greater than Au, greater than Ag, greater than Sn; Mg, Cd, Zn, Sn, Ni, H (in $\text{HCl}$ ) inactive; Cu 100 times more active than Co and Mn.	Cook: <i>J. Gen. Physiol.</i> , <b>10</b> , 189 (1926).
Oxidation of cresol and products obtained at high temp.	$\text{ThO}_2$ .	Sengoku: <i>J. Pharm. Soc. Japan</i> , <b>53</b> , 177-182 (1933).
Oxidation of hydroquinone.	Mn.	Sym: <i>Ann.</i> , <b>487</b> , 174-196, (1931).
Oxidation of xylene to toluic acid; T. $400^\circ$ .	Active silicic acid.	I. G. Farbenindustrie A.-G.: (Mittasch and Luther): G.P. 520,828 (1931).
Oxidation of hydroquinone to quinhydrone to quinone; with compressed $\text{O}_2$ to thymoquinone to thymoquinone.	Gas-activated charcoal.	Gandini: <i>Gazz. chim. ital.</i> , <b>63</b> , 9 (1933).
Oxidation of pyrogallol with $\text{H}_2\text{O}_2$ to a dye; for the formation of a molecule of dye, 2-50 atoms are necessary; retardation (after 8-10 min.) of catalytic activity by the reaction product takes place.	Fe.	Wassermann: <i>J. Chem. Soc.</i> , 1935, 826-828.

Table 27 (Continued).

Reaction	Catalyst	Observer
Oxidation of dibenzyl to benzoic acid; T. 200-300°. $C_6H_5CH_2 \cdot CH_2 \cdot C_6H_5 + 5O \rightarrow 2C_6H_5COOH + H_2O$	MnO <sub>2</sub> or FeO and alkali or alkali carbonates; NaOH.	Union Carbide Co.: U.S.P. 1,463,255 (1923). U.S.P. 1,502,941 (1924). Can. P. 238,730 (1924). F.P. 565,153 (1923).
Oxidation of aromatic hydrocarbons and their derivatives with air.		Maxted: <i>J. Soc. Chem. Ind.</i> , <b>47</b> , 101-105 (1928).
Oxidation of aromatic hydrocarbons.	Al.	Maria Casale: F.P. 638,323, May 22, 1928.
Oxidation of phenols with H <sub>2</sub> O <sub>2</sub> .		Karr: <i>J. Indian Chem. Soc.</i> , <b>14</b> , 291-319 (1937).
Oxidation of phenol with O <sub>2</sub> in H <sub>2</sub> O and H <sub>2</sub> SO <sub>4</sub> of varying conc.; only one atom of O <sub>2</sub> enters the reaction; no chain process; the presence of H <sub>2</sub> SO <sub>4</sub> increases the degree of oxidation of phenol; an increase in acid conc. increases the degree of oxidation.	MnSO <sub>4</sub> .	Kaschtanow and Oleschtschuk: <i>Zhur. Obshchei Khim.</i> , <b>7</b> (69), 1413-1416 (1937).
Oxidation of benzanthrone to benzanthrone.	20% CuO+5% CeO <sub>2</sub> on active charcoal; activated charcoal with H <sub>3</sub> PO <sub>4</sub> +K bisulfate solution improves the catalyst.	I. G. Farbenindustrie A.-G. (Wulff and Dorrer): G.P. 596,592 (1934).
Oxidation of dibenzyl to benzoic acid.	Platinized tin or Pt sponge; acts catalytically only in the presence of H <sub>2</sub> O; MnO <sub>2</sub> has no influence.	Beresowskaja and Ssemichatowa: <i>Zhur. Fiz. Khim.</i> , <b>6</b> , 114-124 (1935).
Oxidation of aromatic cpds. with air: pyridine, T. 600-450°; quinoline, T. 500° (starts to react with O <sub>2</sub> ); carbazol, T. 600° (part of it is oxidized completely to its end product), naphthalene derivatives: $\alpha$ -bromonaphthalene $\alpha$ -naphthylamine $\alpha$ -nitronaphthalene $\beta$ -naphthol oxidized by a stream of air heated to 130-180° and passed over the catalyst at 400 or 420°; oxidation independent of the kind and position of the substituents at the substituted ring; this oxidation differs from that with chromic acid or permanganate.	A mixture of: 90% V <sub>2</sub> O <sub>5</sub> 10% UO <sub>3</sub> on pumice (20-25%).	Salkind and Kessarew: <i>Zhur. Obshchei Khim.</i> , <b>7</b> , (69), 879-881 (1937).
Oxidation of polynuclear aromatic hydrocarbons, especially naphthalene in vapor phase with an oxidizing gas, especially air at 250-350°; at 450-550° mixture led over a less active accelerator with external cooling, and finally with equal cooling over a highly active accelerator; naphthalene oxidized to phthalic anhydride.	Highly active vanadium oxide accelerator.	Solvay Process Co. (Atmospheric Nitrogen Corp.) Can. P. 375,985, Aug. 23, 1938.
Oxidation of aliphatic and aromatic hydrocarbons: $CH_4 \rightarrow HCHO$ $CH_3OH \rightarrow HCHO$ ; isopropanol to acetone; benzene to maleic acid; naphthalene to phthalic acid; anthracene to anthraquinone.	The ash of a mineral oil or mineral oil products containing vanadium is brought upon a carrier.	N. V. de Bataafsche Petroleum Mij (Janssen): Dutch P. 143,508, July 15, 1938.

Table 27 (Continued).

Reaction	Catalyst	Observer
Oxidation of benzine and kerosene, or their mixture; improved by the addition of 0.001-0.085% of one or more organo-metallic compounds which, by the action of the motor, form a catalytically active precipitate of a metal, a metal oxide, or a metal carbonate in the combustion chamber; especially suitable are: Se, Sb, As, Bi, Cd, Te, Th, Sn, Ba, B, Cs, Di, La, K, Na, Ta, Ti, W, and Zn salts of $\beta$ -diketones, e.g., the corresponding propionyl acetone; likewise the metal compounds of naphthenic acids of monoalkyl esters of salicylic, phthalic, or malonic acid, cresol or other phenols, mercaptans, acetoacetic acid esters, high molecular weight saturated and unsaturated fatty acids, and aryl carbonic acids.		Leo Corporation (Lyons and McKone); U.S.P. 2, 151,432, March 3, 1939.

## PART XI

## Catalytic Hydrogenation in Organic Chemistry

Table 1. Catalytic Preparation of Hydrogen.

Reaction	Catalyst	Observer
Preparation of $H_2$ from $H_2O$ in the presence of suitable scrap Fe; T. 300-350°; pressure 250-300 atm. $3Fe + 4H_2O \rightarrow 4H_2 + Fe_3O_4$ (3000 cu ft. of $H_2$ per day can be obtained from a bomb of ten gallon capacity).	Small amounts of ferrous salts and copper.	Bergius: <i>J. Soc. Chem. Ind.</i> , <b>32</b> , 462 (1913). Bergius: G.P. 254,593 (1911). G.P. 277,501 (1913). G.P. 286,961 (1913).
Preparation of $H_2$ ; preliminary heating (up to 400°) of $H_2$ mixed with small amounts of CO or $O_2$ over catalysts with a cleansing action; $H_2$ heated in heat exchangers by inert gases, such as $N_2$ (in a separate stream); inert gas itself heated in tubes by flame or by melted metals of the 8th group.		Gas Verarbeitung Gesellschaft: E.P. 307,027, April 24, 1929.
Preparation of $H_2$ by the decomposition of hydrocarbons in the presence of water vapor, $CO_2$ , or $O_2$ .	A mixture of Fe, Ni, Co with $O_2$ -containing Al compounds and one or more elements: Si, H <sub>2</sub> , C, B, P; e.g., Al silicate, bauxite, kaolin; the catalysts may also contain alkaline-earth oxides.	I. G. Farbenindustrie A.-G.: E.P. 323,855, Feb. 6, 1930. F.P. 677,826 (1931).
Preparation of $H_2$ and $H_2-N_2$ mixtures.		Glund, Keller, Klempt and Bestehom: <i>Ber.</i> <b>63</b> , 211-370 (1930).
Preparation of $H_2$ in the presence of water vapor and CO in the ratio 1.5:1 over catalysts; T. above 300°.	Catalysts containing Cu and one or more oxides of Zn, W, Cr, Mo, Zr, V, Mn, U, Mg.	Lazote, Inc.: F.P. 674,475, Jan. 29, 1930.
Preparation of $H_2$ ; water vapor and CO led at 500° over a catalyst heated in a non-oxidizing atmosphere of 200°.	Cr oxide gel.	Dupont Ammonia Corporation (Beekley): U.S.P. 1,789,538, Jan. 20, 1931.
Preparation of $H_2$ for hydrogenation.		Armstrong: <i>Trans. Inst. Chem. Engrs. (London)</i> , <b>9</b> , 139-157 (1931).
Preparation of $H_2$ by water gas reaction ( $CO : H_2O = 1 : 3$ ).	$Fe_2O_3$ (prepared by precipitation from a $Fe(NO_3)_3$ solution to which $NH_3$ has been added and igniting the dried precipitate at 350° carbide formation; $Fe_2O_3$ reduced to $Fe_3O_4$ ; greatest ac-	Joshimura: <i>J. Soc. Chem. Ind. Japan</i> , <b>34</b> , 193B-195B (1931).

Table 1 (Continued).

Reaction	Catalyst	Observer
	<p>tivity at 450°; magnetic conversion point of <math>\text{Fe}_2\text{O}_3</math> may influence the catalytic action at 530° in addition to the chemical changes; at 800° rapid decrease in rate of reaction; at 600°, reaction constant; oxidation of CO, yield 85%; the lower the temp. the greater the amount of C precipitated.</p>	
Preparation of $\text{H}_2$ by water gas reaction.	<p>The catalytic activity of <math>\text{Cr}_2\text{O}_3</math> and <math>\text{Al}_2\text{O}_3</math> is half that of <math>\text{Fe}_2\text{O}_3</math> at 500°, equals it at 600°, exceeding it at 800°; no decrease in activity with time; <math>\text{Al}_2\text{O}_3</math> considerably less active at low temp. than <math>\text{Cr}_2\text{O}_3</math> and <math>\text{Fe}_2\text{O}_3</math>; maximum activity: <math>\text{Fe}_2\text{O}_3</math>, 450°, <math>\text{Cr}_2\text{O}_3</math>, 550° <math>\text{Al}_2\text{O}_3</math>, 1000°; the activity of a mixture (50-50) of <math>\text{Fe}_2\text{O}_3</math> and <math>\text{Cr}_2\text{O}_3</math> is greater than may be anticipated; at 450° activity of <math>\text{Cr}_2\text{O}_3</math> alone is less; 5-7% <math>\text{Cr}_2\text{O}_3</math> sufficient for action.</p>	
Preparation of $\text{H}_2$ by water gas reaction.	<p>The effect of <math>\text{Cr}_2\text{O}_3</math> on the activity of <math>\text{Fe}_2\text{O}_3</math>; decrease in activity of <math>\text{Fe}_2\text{O}_3</math> in water gas reaction very rapid above 800°, which may be prevented by the addition of 7 mol % <math>\text{Cr}_2\text{O}_3</math>; amount C precipitated from CO decreased; formation of a solid solution or a spinell between <math>\text{Fe}_2\text{O}_3</math> and <math>\text{Cr}_2\text{O}_3</math> assumed.</p>	<p>Joshimura: <i>Chem. News</i>, <b>143</b>, 267-268, (1931).          Joshimura: <i>J. Soc. Chem. Ind. Japan</i>, <b>34</b>, 271B-273B (1931); <b>35</b>, 85B-88B (1932).</p>
Preparation of $\text{H}_2$ by decomposition of saturated or unsaturated hydrocarbons higher than methane below 1000° in the presence of water vapor or $\text{CO}_2$ .	<p>One or more metals of the Fe group (Fe, Co, Ni) precipitated in the presence of activating substances, Al or Mg (hydraulic binding materials).</p>	<p>I. G. Farbenindustrie A.-G.: F.P. 729,119, July 19, 1932.</p>
Preparation of $\text{H}_2$ by decomposition of hydrocarbons below 1000° in the presence of water vapor; formation of lampblack avoided by using two catalysts of varying activity, the most active catalyst following the least active.	<p>Precipitated hydrates of Ni and Al with 60% Al cement; precipitated Ni carbonate, kaolin and magnesia.</p>	<p>I. G. Farbenindustrie A.-G.: F.P. 729,429, July 23, 1932.</p>
Preparation of $\text{H}_2$ by decomposition of hydrocarbons in tubes filled with a catalyst in the presence of water vapor.	<p>Material of apparatus: alloys containing equal amounts of Ni and Cr; 20 to 24% may be used on inert carriers.</p>	<p>Tröger: <i>Petroleum Age</i>, <b>28</b> (34), 9-11 (1932).</p>
Preparation of $\text{H}_2$ from a gas mixture containing a hydrocarbon and water vapor; between single reaction stages the lowered temp. is again increased to that required.	<p>Many contacts of the same composition added one after another.</p>	<p>Atmospheric Nitrogen Corporation: U.S.P. 1,874,801, Aug. 30, 1932.</p>
Preparation of $\text{H}_2$ from $\text{CH}_4$ , $\text{C}_2\text{H}_6$ or $\text{C}_2\text{H}_4$ or their mixture; T. above 800°.	<p>Mixtures of metal oxides of the Fe group (Fe, Co, Ni) with acid-forming metal oxides of the 4th, 5th, or 6th groups; oxide mixtures should have vapor-like properties corresponding to a temp. of 800°.</p>	<p>N. V. de Bataafsche Petroleum Mij.: F.P. 731,652, Sept. 6, 1932.</p>
Preparation of $\text{H}_2$ or fuel gases by the catalytic decomposition of hydrocarbons with water vapor; T. above 450°; pressure normal, decreased or increased.	<p>Ni, Co, or Fe (prepared by reduction of their respective cpds.)</p>	<p>Witkiewicz, Patryś and Ziolkowski: Polish P. 16,033, June 15, 1932.</p>

Table 1 (Continued).

Reaction	Catalyst	Observer
Preparation of $H_2$ by water gas reaction.	$Fe_2O_3$ (sensitive to heat); no essential change in its activity by heating to $600^\circ$ ; $Fe_2O_3$ containing only 0.071% Mn, after 4 hours heating up to $780^\circ$ , loses practically all its activity for the oxidation of CO; a catalyst containing small amounts Si, Cu, Al, Cr, Mn, Ni, Ca, S, P, retains its activity up to $780^\circ$ ; no differences in activity observed between similar catalysts ( $Fe_2O_3$ — $Cr_2O_3$ ) heated to $750^\circ$ and rapidly cooled to $50^\circ$ and those cooled slowly; irreversible irregularities of the heat-treated catalyst cannot be due to magnetic changes.	Joshimura: <i>J. Soc. Chem. Ind. Japan</i> , 36, 306B-368B (1933).
Preparation of $H_2$ in the presence of water vapor.	Raschig rings.	Hobler, Zwislocka and Zwislocki: Polish P. 17,916, April 18, 1933.
Preparation of $H_2$ in the presence of water vapor and $CO_2$ -containing gases; T. $300$ – $350^\circ$ .	Ni and Fe; a suitable catalyst consists of Fe, Ni and Cr; Ni content of catalyst preferably 15–25%, but may be increased to 60%.	I. G. Farbenindustrie A.-G.: F.P. 740,663, Jan. 30, 1933.
Preparation of $H_2$ in the presence of water vapor and $CO_2$ -containing gases; temp. above decomposition temp. of $MgCO_3$ , but not above $500^\circ$ .	A mixture of an alkali carbonate and an excess of $MgO$ and/or $Mg(OH)_2$ or $MgCO_3$ ; also charcoal; 70–80% charcoal and 20–30% of a mixture of $MgO$ and alkali carbonate, 3:1 to 5:1 ratio.	Oesterreich-American Magnesite A.-G. (Hausging): Austrian P. 7,516, Sept. 28, 1933.
Preparation of $H_2$ by the decomposition of hydrocarbons in the presence of water vapor.	Fe, Ni, Zn, Co; solutions of $Ni(NO_3)_2$ or $Co(NO_3)_2$ treated with Mn-, Ca-, Ba-, Sr-, or $Mg(OH)_2$ carbonates or oxalates.	Dupont (Woodhouse): U.S.P. 1,959,189, May 15, 1934.
Preparation of $H_2$ by water gas reaction; T. $450^\circ$ .	$Fe_2O_3$ ; mechanically pressed $Fe_2O_3$ — $Cr_2O_3$ (10 mol % $Cr_2O_3$ ); the mixture shows no decrease in activity when heated for 10 min.; $Cr_2O_3$ uniformly distributed in $Fe_2O_3$ (mixed crystal formation assumed); treatment involves passing $H_2O$ into $Fe_2O_3$ , but not into $Fe_2O_4$ ; drying and heating for 70 hrs. at $300$ – $350^\circ$ .	Joshimura and Sugimoto: <i>J. Soc. Chem. Ind. Japan</i> , 37, 182B–183B (1934).
Preparation of $H_2$ by decomposition of hydrocarbons in the presence of poison-free gases (water vapor, air, $N_2$ , $H_2$ ) heated to $900$ – $1050^\circ$ for 12 to 72 hours; T. $1000^\circ$ .	Mixtures of the Fe group with metals or compounds of difficultly reducible oxides.	Standard Oil Development Co. (Hanks, Freyermuth and Potte): U.S.P. 2,028,326, Jan. 21, 1936.
Preparation of $H_2$ by water gas reaction.		A. van der Werth: <i>Chem. Ztg.</i> , 59, 276–277 (1935).
Preparation of $H_2$ by decomposition of $CH_4$ in presence of water vapor.	Ni salt is added to a carrier, such as pumice, $MgO$ , or burnt dolomite, in aqueous hydroxide (alkali) solution with stirring; during precipitation (complete) a pH of 11–14 is maintained; the ppt. is separated, washed and dried.	Atmospheric Nitrogen Corporation (Porter): U.S.P. 2,013,066, Sept. 3, 1935.
Preparation of $H_2$ , as well as $H_2$ -containing gases, by decomposition of mineral coal with water vapor in a superheated atmosphere (gases set free and containing $H_2O$ are conducted twice through a layer of hot coals).	Catalysts may be used.	I. G. Farbenindustrie A.-G.: F.P. 801,380, Aug. 3, 1936.



Table 1 (Continued).

Reaction	Catalyst	Observer
Preparation of atomic H <sub>2</sub> ; evaporation of atoms from a very thin adsorbed layer, or a process in which H <sub>2</sub> molecules collide with heavy W atoms causing a splitting is assumed to take place; both cases indicate a proportionality of $n$ (number of original W atoms/sec. on g./cm. <sup>2</sup> of glowed W wire) with $\sqrt{p}$ ; this experiment does not decide which of the two possibilities is correct.	Hot tungsten wire.	Roberts and Bryce: <i>Proc. Cambridge Phil. Soc.</i> , <b>32</b> , 653-656 (1936).
Preparation of H <sub>2</sub> by decomposition of hydrocarbons, such as CH <sub>4</sub> in the presence of H <sub>2</sub> O; T. 450-800°.	Pd and Mg, Be, Ti, Th, Ce, or W oxides and Cr <sub>2</sub> O <sub>3</sub> , e.g., 95.5% CeO <sub>2</sub> , 2.5% Pd, 2.0% Cr <sub>2</sub> O <sub>3</sub> . (Pd is precipitated in an alkaline medium of pH = 11 or higher upon metal cmpds.).	Atmospheric Nitrogen Corporation (Rewal): U.S.P. 2,030,283, Feb. 11, 1936.
Preparation of H <sub>2</sub> by decomposition of hydrocarbons in the presence of water vapor; T. about 1600°F. CH <sub>4</sub> + H <sub>2</sub> O → CO + 3H <sub>2</sub>	Ni powder + Mg pyrophosphate: 5-50% Ni and 20-75% Mg.	Standard I. G. Co. (Small): U.S.P. 2,084,511, June 22, 1937.
Preparation of H <sub>2</sub> from gas waste in coal hydrogenation with water vapor; T. increasing from 250-600° to 1400-1700°.	Heat-retaining substances, such as MgO, or lignite, or pieces of coke.	I. G. Farbenindustrie A.-G.: E.P. 458,692, Jan. 21, 1937.
Preparation of H <sub>2</sub> by oxidation of CH <sub>4</sub> in the presence of water vapor.	Ni(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O is dissolved in water to which is added H <sub>3</sub> PO <sub>4</sub> ; MgO is added slowly to the solution; the paste obtained is dried at 455-475° and the nitrate converted into the oxide; the hot precipitated powder is pressed under pressure of 700 kg./sq. cm. and heated to 920-1090°; the oxide may likewise be reduced by H <sub>2</sub> to the metal; the catalyst obtained is of high mechanical rigidity.	International Hydrogenation Patents Co., Ltd.: F.P. 818,078, Sept. 17, 1937.
Preparation of H <sub>2</sub> from solid, liquid or gaseous fuels by combustion in a generator in the presence of water vapor so that a gas with 5-15% CO is obtained; after removing CO <sub>2</sub> by washing at normal or elevated pressure, CO with water vapor is converted into H <sub>2</sub> over the catalyst and CO <sub>2</sub> at elevated temp., and CO <sub>2</sub> removed as usual; the H <sub>2</sub> gas contains only 0.8% CO as impurity.	MgO and ZnO.	I. G. Farbenindustrie A.-G.: F.P. 820,804, Nov. 19, 1937.
Preparation of H <sub>2</sub> ; CH <sub>4</sub> with an excess of H <sub>2</sub> O vapor converted into H <sub>2</sub> (0.9%); T. 1525°F.	Difficultly reducible oxide (MgO) is impregnated with a solution of Ni(NO <sub>3</sub> ) <sub>2</sub> ; mixture dried at such high temp. that the nitrate becomes the oxide; the latter is pressed into tablets and reduced to the metal (the tablets are very active).	Standard Oil Development Co. (Swaney and Spieer): U.S.P. 2,125,743, Aug. 2, 1938.
Preparation of H <sub>2</sub> by treating a mixture of S-containing or S-mixed hydrocarbons; T. 1500°F. (the mixture of CH <sub>4</sub> and higher hydrocarbons with 10% olefins obtained by cracking petroleum oil is led over the catalyst with 7% H <sub>2</sub> and 1% S with 200% vapor); yield, 3.4% CO <sub>2</sub> ; 7.8% CO; 55.5% H <sub>2</sub> ; 29.4% CH <sub>4</sub> and 3.8% C <sub>2</sub> H <sub>4</sub> .	80% W oxide and 20% MgO treated at 750°F. for 12 hrs. with H <sub>2</sub> S.	Standard Oil Development Co. (Spieer and Davis): U.S.P. 2,135,058, Nov. 1, 1938.

Table 1 (Continued).

Reaction	Catalyst	Observer
Preparation of $H_2$ and $CO_2$ from hydrocarbons.	NiO (finely divided reducible metal oxide) is mixed with Cu or Fe (finely divided metal) and the mixture made into globules; the catalytic substance should thereby diffuse into the metal and alloy with it; the temp. must be chosen so that the metal does not sinter nor convert all the initial substance into the alloy.	Jeunes: U.S.P. 2,136,509, Nov. 15, 1938.

Table 2. Catalytic Hydrogenation of Carbon Monoxide.

Reaction	Catalyst	Observer
Hydrogenation of CO; T. 300–350°; pressure 100 atm.; formation of mixture of alcohols and ethers with water.	Fe, Ni, Co mixed with Th or Cd (metals as nitrates ignited and reduced).	I. G. Farbenindustrie A.-G.: E.P. 300,294 (1928).
Hydrogenation of CO to alcohols higher than methanol.		Frolich and Cryder: <i>Ind. Eng. Chem.</i> , <b>22</b> , 1051–1057 (1930).
Hydrogenation of CO; T. 367°; conversion point at 372°; conversion temp. curve shows a "jump."	Ni, Ni-Cu, Co-Ni; for pure Ni (5%), the magnetic conversion point lies at 368°; for Ni-Cu (15%) at 200°; it is believed that magnetic conversion influences catalytic activity.	Fischbeck and Salzer: <i>Z. Elektroch.</i> , <b>41</b> , 158–169 (1935).
Hydrogenation of CO at atmospheric pressure.	Fe-Cu (prepared by precipitation from a Fe-Cu nitrate solution); kieselguhr acts unfavorably as a carrier; addition of $K_2CO_3$ is necessary; x-ray analysis indicates the presence of magnetite ( $Fe_3O_4$ ), rhombic $Fe_2O_3$ and Fe; Cu causes reduction of $Fe_2O_3$ at low temp., activates and stabilizes it; therefore Cu should be taken only in small amounts.	Antheaume: <i>Ann. combustibles liquides</i> , <b>10</b> , 473–507 (1935).
Hydrogenation of CO; T. greater than 200°; high pressure.	Zn : Cu : Cr = 60 : 30 : 10 Zn : Cu : Cr = 45 : 10 : 45 Zn : Cu = 2 to 2-4½ : 1; the latter catalyst very stable to temp.	Karpen & Bros. (Dodge): U.S.P. 2,014,883, Sept. 17, 1935.
Hydrogenation of CO ( $CO : H_2 = 2 : 1$ ); T. 220–320°; pressure, 12 atm.	Precipitated $Fe(OH)_3$ heated with addition of 5% $Al(OH)_3$ in a stream of $H_2$ at 850°; or decomposition of nitrates of Fe, Ni, Co which may contain $SiO_2$ , kieselguhr, Cu, Mn, W, Cr, Mo, Th.	I. G. Farbenindustrie A.-G.: Ital. P. 345,671, Nov. 2, 1936. F.P. 814,636, June 26, 1937. F.P. 812,290, May 4, 1937.
Hydrogenation of CO and $CO_2$ to methanol.	Substances obtained by partial or complete pyrogenetic decomposition of organic salts of Zn (acetate) or Fe at temp. lower than their decomposition temp. under increased pressure with elimination of air in inert gas atmosphere.	Natta: Ital. P. 342,930, June 10, 1936.
Hydrogenation of CO ( $CO : H_2 = 50 : 50$ ) to oil (73 cc.) and hydrocarbons (155 cc.) liquefying at 80° under normal pressure; T. 370–410°; pressure 75–80 atm.	A mixture of: (A) 1000 g. Fe pdr. (obtained by decomposition of Fe carbonyl) 50 g. uranyl nitrate 50 g. $TiO_2$ (melted, cooled, powdered and reduced with $H_2$ at 460°) (B) 1000 g. Fe pdr. 50 g. Si pdr. 50 g. molybdic acid 1 g. NiO 50 g. KOH (dissolved in 50 cc. $H_2O$ )	I. G. Farbenindustrie A.-G.: F.P. 812,290, May 4, 1937. E.P. 465,668, June 10, 1937. Ital. P. 345,513, Oct. 24, 1936.
Hydrogenation of CO to methanol	Charcoal and Fe filings.	Societa Anonima Prodotti Italiana Sintesi: F.P. 814,434, June 23, 1937. Belg. P. 418,643, April 30, 1937.

Table 2 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of CO to gaseous, liquid and solid hydrocarbons and their O <sub>2</sub> -containing derivatives.	Contact surface of Fe (etched).	I. G. Farbenindustrie A.-G. (Linckh and Winkler); Can. P. 371,802, Feb. 8, 1938.
Hydrogenation of CO (atmospheric pressure) in hydrocarbon synthesis according to Fischer.	Fe <sub>2</sub> O <sub>3</sub> activity may be increased considerably if K <sub>2</sub> CO <sub>3</sub> is permitted to adsorb on the precipitated Fe hydroxide; the same effect is obtained if K <sub>2</sub> CO <sub>3</sub> is replaced by the carbonates of Na, Li, Rb, or Cs, or Be nitrate; all these catalysts give the same thermomagnetic curves; it is believed that, not the ferrite, but the cubic form of Fe <sub>2</sub> O <sub>3</sub> is the active substance, because of hydrolysis of the catalyst, whereby the ferrite is disintegrated; this does not injure catalytic activity; but if the hydrolyzed product is temporarily heated above 500°, whereby the cubic form of Fe <sub>2</sub> O <sub>3</sub> changes into the rhombic, then the catalytic activity decreases considerably; simultaneously the Curie Point of the cubic Fe <sub>2</sub> O <sub>3</sub> disappears; thus it is assumed that the action of additions consists in the stabilization of the cubic form of Fe <sub>2</sub> O <sub>3</sub> ; the catalyst has the best activity in the Curie Point of the cubic Fe <sub>2</sub> O <sub>3</sub> (250°); the yield here is 80 g. solid and liquid hydrocarbons per cbm. CO + 2H <sub>2</sub> mixture.	LeClerc: <i>Compt. rend.</i> , <b>207</b> , 1099-1101 (1938).
Hydrogenation of CO; T. 175°; likewise, conversion of H <sub>2</sub> with benzene or acetone which proceeds smoothly to cyclohexane, as well as to isopropanol, using the cubic form of Ni, but not the hexagonal form; a mixture of C <sub>2</sub> H <sub>4</sub> and H <sub>2</sub> reacts in the cold, with development of heat and change in volume in the presence of cubic Ni; no change with hexagonal Ni; in comparison with hexagonal Co as catalyst, hexagonal Ni is inactive; from this fact it is deduced that catalytic activity is concomitant with ferromagnetism and that the former is closely related to the electronic structure.	Ni (cubic form) Ni (hexagonal form) (by prolonged heating to 250° in a vacuum, or with Na, Ni may revert into the cubic-ferromagnetic form and the catalytic properties be reestablished).	LeClerc and Lefebvre: <i>Compt. rend.</i> , <b>208</b> , 1650-51 (1939).

Table 3. Catalytic Hydrogenation of Carbonyl Compounds.

Reaction	Catalyst	Observer
Hydrogenation of carbonyl compounds to alcohols.	Raney's Ni covered with metals of the Pt group (Pt or Ir) in the presence of NaOH; 4.5 g. Ni mechanically shaken with 50 cc. H <sub>2</sub> O; after 10 min. a dilute solution of a noble metal (salt of an alkali chloride) is added, the liquid decanted, the metal washed with 100 cc. H <sub>2</sub> O, then with alcohol, and suspended in 60 cc. of alcohol, when it is added to the substances to be hydrogenated; 0.1 g. noble metal adsorbs H <sub>2</sub> in 3 min., after which 10N NaOH is added and hydrogenation carried out until adsorption stops at room temp. and atm. pressure; after addition of NaOH, adsorption velocity increases considerably and decreases only when 2/3 of H <sub>2</sub> is combined.	Delépine and Horeau: <i>Compt. rend.</i> , <b>202</b> , 995-998 (1936). Delépine and Horeau: <i>Bull. soc. chim.</i> (5), <b>4</b> , 31-49 (1937).

Table 3 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of 1 mol Ni carbonyl with 4 mols $H_2$ ; T. 25–400°; pressure, 1–75 atm. $H_2$ ; decomposition of Ni carbonyl and formation of $CO_2$ , $CH_4$ and $H_2O$ take place; the same compds. are obtained by hydrogenation of CO; reaction mechanism determined by water formation followed by the reaction: $2C + 2H_2O \rightarrow CO_2 + CH_4$ elemental C reacts considerably only if Ni is present as a catalyst; T. 250°.	Ni.	Litkenhaus and Mann: <i>Ind. Eng. Chem.</i> , 29, 934–938 (1937).

Table 4. Catalytic Hydrogenation of Ethylene.

Reaction	Catalyst	Observer
Hydrogenation of $C_2H_4$ .	Ni. Co.	G.P. 262,541, Kl 12o, Gr 1, Aug. 11, 1910.
Hydrogenation of $C_2H_4$ .	Colloidal Pt.	Skita and Meyer: <i>Ber.</i> , 45, 3879–3895 (1912).
Hydrogenation of $C_2H_4$ .	Ni.	Kather and Reid: <i>J. Am. Chem. Soc.</i> , 37, 2115–2118 (1915). Chemische Fabrik Griesheim Elektron A.-G.: G.P. 350,429, Kl 12o, March 20, 1922. Taylor: <i>J. Franklin Inst.</i> , 194, 1–27 (1922).
Hydrogenation of $C_2H_4$ .	Cd + Zn (slight activity explained by occurrence of recrystallization).	G.P. 292,894, June 29, 1916.
Hydrogenation of $C_2H_4$ .	Ni : $Al_2O_3$ = 100 : 2.5.	Skärblom: <i>Tek. Tid. (C)</i> , 62, 57–60
Hydrogenation of $C_2H_4$ .	Finely divided Ni.	Foresti: <i>Gazz. chim. ital.</i> , 54, 132–146 (1924).
Hydrogenation of $C_2H_4$ .	Ni cpds. with $SiO_2$ .	Schicht and Mielck: Austrian P. 88,453, May 10, 1922.
Hydrogenation of $C_2H_4$ .	Metallic Cu.	Pease: <i>J. Am. Chem. Soc.</i> , 45, 1196–1210 (1923). Pease and Harris: <i>Ibid.</i> , 49, 2503–2510 (1927).
Hydrogenation of $C_2H_4$ .	Ca.	Pease and Stewart: <i>Ibid.</i> , 47, 1235–1240, 2763–2766 (1925).
Hydrogenation of $C_2H_4$ .	Cu (poisoned with CO).	Griffin: <i>Ibid.</i> , 49, 2136–2145 (1927).
Hydrogenation of $C_2H_4$ to $C_2H_6$ .	Silicic acid.	Morris and Reyerson: <i>J. Phys. Chem.</i> , 31, 1220 (1927)
Hydrogenation of $C_2H_4$ to $C_2H_6$ ; T. 200°; yield, 98%.	Ni- $Al_2O_3$ - $ThO_2$ suspended in paraffin oil.	Fischer and Peters: <i>Brennstoff-Chem.</i> , 12, 286 (1931).
Hydrogenation of $C_2H_4$ .	Activated charcoal.	Schuster: <i>Z. Elektroch.</i> , 38, 614 (1932).
Hydrogenation of $C_2H_4$ ; T. 480°.	$MoO_3 \cdot ZnO$ .	I. G. Farbenindustrie A.-G.: E.P. 372,496, June 2, 1932.
Hydrogenation of $C_2H_4$ .	Cu on kieselguhr (previous adsorption of $H_2$ favors hydrogenation; previous adsorption of $C_2H_4$ hinders hydrogenation).	Harker: <i>J. Soc. Chem. Ind.</i> , 51T, 326 (1932).
Hydrogenation of $C_2H_4$ .	Platinized wire; Pt black.	Tauber: <i>Z. physik. Chem. (B)</i> , 19, 97–101 (1932).
Hydrogenation of $C_2H_4$ .	Active charcoal containing Ni.	Schuster: <i>Chem. Age (London)</i> , 26, 46, (1932).
Hydrogenation of $C_2H_4$ .	Thin layers of Ag, Zn and Cd (T. 15–100°); Cd + Zn showed slight activity explained by recrystallization.	Dankow and Dobytschin: <i>Zhur. Fiz. Khim.</i> , 4, 343–345 (1933).

Table 4 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of $C_2H_4$ to $C_2H_6$ .	Layers of Ni, Fe and Pt metals $\sim 10^{-4}$ cm. with ultramicroscopic structure (maximum $15\text{--}20\text{ }\mu$ ), obtained by evaporation and condensation in vacuum; the activity of a layer of Ni with a thickness below $2\text{ }\mu$ is zero, but increases rapidly when it approaches $30\text{ }\mu$ ; influence of carriers, such as glass, brass, paper and mica on the activity of the catalyst, not observed; Ni and Fe not active when exposed to air; Pt, unchanged; Ni and Fe undergo fatigue; activation values calculated with respect to the mass of the catalyst; depending on the thickness of the layer, Ni shows a sharp maximum in the region $15\text{--}20\text{ }\mu$ ; parallel with anomalous electrical conductivity of the metal layer.	Dankow: <i>Ibid.</i> , <b>4</b> , 326-333 (1933)
Hydrogenation of $C_2H_4$ ; T. $100\text{--}130^\circ$ ; reaction velocity at low temp. is independent of the pressure of $C_2H_4$ ; at higher temp., about linearly dependent; $C_2H_4$ reacts with $H_2$ ; after adsorption proceeds rapidly on active centers of contact surface; hydrogenation is slowest phase of the process.	Ni ribbon.	ZurStrassen: <i>Z. physik. Chem. (A)</i> , <b>169</b> , 81-90 (1934).
Hydrogenation of $C_2H_4$ to alcohol; T. $150\text{--}300^\circ$ ; normal pressure.	Cd phosphate (best), alumina, acid activated alumina types.	Weinscheid and Kaganowa: <i>Russ. P.</i> 38,143, Aug. 8, 1933; (Refer to C. 1935 II 2580).
Hydrogenation of $C_2H_4$ to alcohol; T. $275^\circ$ (optimum); pressure, 50 atmospheres; yield, 2%* and 3.5%†.	Pt black, $Ag_2SO_4$ , $ThO_2$ (activity, slight), $Al_2O_3$ + 10 mol % $ZnO$ *; Russian kaolin.†	Frost: (Refer to C. 1931 I 2034).
Hydrogenation of $C_2H_4$ oxides in alcoholic solution until the calculated amount of $H_2$ is adsorbed; T. $35\text{--}45^\circ$ .	Ni (prepared from $NiCO_3$ in a stream of $H_2$ at $280\text{--}325^\circ$ ).	Weill and Kayser: <i>Bull. soc. chim. (5)</i> , <b>3</b> , 841-844 (1936).
Hydrogenation of $C_2H_4$ ; T. $0^\circ$ (industrial process).	Prepared by mutual precipitation of $Cu(OH)_2$ and $Mg(OH)_2$ in the ratio of 1 : 4 and reduction of the washed and dried precipitate in a stream of $H_2$ .	Taylor and Joris: <i>Bull. soc. chim. Belg.</i> , <b>40</b> , 241-252 (1937).
Hydrogenation of $C_2H_4$ to $C_2H_6$ ; the amount of $C_2H_6$ is proportional to the partial pressure of $C_2H_4$ in the starting gas and the percentage conversion is independent of the initial mixture.	Cu-Ag alloys; activity depends on the grain size of crystallites and on length of the phase boundary; pure metals are poor catalysts and their activation energy is greatly decreased by admixing another metal (within solubility limit); from 27 to 17 k. cal. for Ag and Ag+3% Cu.	Rienäcker and Bommer: <i>Z. anorg. allgem. Chem.</i> , <b>236</b> , 263-270 (1938).
Hydrogenation of $C_2H_4$ ; constant volume; T. $-40$ and $-89^\circ$ ; adsorption curves taken for $C_2H_4$ , $C_2H_6$ and $H_2$ on pure Fe; activation energy in hydrogenation is between 5 and 7000 cal.; hydrogenation proceeds faster on pure than on promoted catalyst; therefore $C_2H_4$ hydrogenation is hindered by surface conditions which promote formation of $NH_3$ ; the activated adsorption of $H_2$ ; namely, the low temp. type of activated adsorption, is significant for hydrogenation; $C_2H_4$ adsorbed physically.	Fe catalysts used in $NH_3$ synthesis; pure Fe and Fe with promoters; 1.6% $K_2O$ and 1.3% $Al_2O_3$ .	Hansford and Emmett: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 1185-1190 (1938).

Table 4 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of $C_3H_4$ ; T. 99° and 165°; kinetics of the reaction described by a constant $H_2$ pressure by the equation: $dx/dt = K_1 \cdot p_{C_3H_4} / (1 + K_2 p_{C_3H_4})$ the reaction order with respect to $C_3H_4$ is slightly smaller than one; at constant pressure of $C_3H_4$ it is expressed: $dx/dt = K_1 \cdot p_{H_2}$ ; the reaction mechanism is assumed to be the same as at lower temp. and the apparent differences are based only on decrease in adsorbed gas as a result of temp. increase; from the temp. coefficient of the constant $K_1$ it follows that the heat of adsorption of $C_3H_4$ is 15 k. cal./mol; $K_1$ is independent of temp.; the true activation heat of the reaction should be about as great as the sum of adsorption heats of both reaction partners.	Ni wire (the catalyst is activated by oxidation and, following reduction, with $H_2$ at 360°).	Toyama: <i>Rev. phys. Chem. Japan</i> 12, 115-124 (1938).
Hydrogenation of ethylene; T. 134° as well as 122°; T. 205° respectively 132°; experimental temp. from room temp. to 300°; experimental pressure 500 mm.; at ordinary temp. within 1 hr. no marked reaction between $H_2$ and $C_2H_4$ takes place, while on a surface-oxidized catalyst a slowly increasing reaction velocity is observed and after 12 hrs. a constant maximum value is attained.	Ni-Cu alloy (with 75% Ni content and 0.3% Mn) tempered at 1200° (without pretreatment of the catalyst); the tempered catalyst is at all temp. considerably more active than untreated catalyst; the catalytic activity of a ferromagnetic substance is greatly increased at the magnetic conversion point; when the magnetic conversion temp. in an alloy containing ferromagnetic substance is lowered, the temp. of maximum catalytic activity decreases correspondingly; by heating the catalyst <i>in vacuo</i> to 170° and cooling to room temp., it becomes very active at once; likewise by pretreatment with $H_2$ at room temp., while treatment with ethylene gas makes it inactive for more than 4 hrs.	Anyama, Matsuzawa and Takahashi: <i>Sci. Papers Inst. Phys. Chem. Research (Tokyo)</i> , 34, 957-80 (1938).
Hydrogenation of ethylene; T. 88-220°.	Mixed Ni-Mo of various crystallographic properties and prepared by different methods; they are formed by reduction of oxide mixtures and consist, as indicated by x-ray analysis, of $MoO_3$ and Ni, which incorporates a part of the elemental Mo present in a solid solution; the active ingredient is assumed to be non-crystalline, i.e., Ni is not in a stable lattice binding ( $MoO_3$ acts only as inert admixture eventually slowing down the diffusion and thus contrary to similar systems studied in the hydrogenation of phenol).	Schwab and Nakamura: <i>Z. physik. Chem. (B)</i> , 41, 189-198 (1938); Refer also to Kingman and Rideal: (Refer to C. 1936 II 2082 and C. 1938 I 815).
Table 5. Catalytic Hydrogenation of Ethylene Derivatives.		
Reaction	Catalyst	Observer
Hydrogenation of hexamethylene and pentamethylene.	Pd black.	Tausz and von Putnoy: <i>Ber.</i> , 52, 1575-83 (1919).
Hydrogenation of propylethylene into pentane.	Ni formate.	Fett Industrie Gesellschaft (Bremen); G.P. 329,471, Kl 120, Gr 27, Jan. 23, 1912.
Hydrogenation of the peroxide of trimethylethylene; pure olefins are difficult to hydrogenate with this catalyst but, as olefins form peroxides readily on	Fe-containing $PtO_2$ ; addition of 0.001 mol furoyl-benzyl or succinyl peroxide decreases the reduction by 40-50%; this action is ascribed also to acids	Thomson: <i>J. Am. Chem. Soc.</i> , 56, 2744-2747 (1934).

Table 5 (Continued).

Reaction	Catalyst	Observer
shaking with air, decompose into acetone and acetaldehyde, the latter oxidizing further to acetic acid, counteracting the retarding influence of Fe; acetaldehyde takes an active part in hydrogenation only after oxidation to acetic acid; with iron-free catalysts, the acids do not act either upon the velocity or capacity of the hydrogenation process; trimethylethylene distilled over Na adsorbs only 27% of the calculated amount of H <sub>2</sub> in alcohol in the presence of PtO <sub>2</sub> containing Fe.	originating in the reduction of peroxides; small amounts of conc. HCl or acetic acid are still more active.	

Table 6. Catalytic Hydrogenation of Diisobutylene.

Reaction	Catalyst	Observer
Hydrogenation of diisobutylene in liquid or gaseous phase; T. 225-275°; pressure slightly in excess 1-2 atm.	Ni, Fe, Co, Cu activated by: 5-15% ThO <sub>2</sub> 1-10% Cr <sub>2</sub> O <sub>3</sub> 10-20% ZrO <sub>2</sub>	International Hydrogenation Patents Co., Ltd.: F.P. 809,347, March 1, 1937.
Hydrogenation of diisobutylene in gaseous phase to the corresponding paraffinic hydrocarbons (isooctane); T. 240-350°; pressure, 35-240 atm.	Fresh Fe oxide, reduced at 300-500°.	Anglo-Iranian Oil Co. (Dunstan): F.P. 818,533, Sept. 28, 1937.
Hydrogenation of diisobutylene in two stages: (1) hydrogenation charge (2) H <sub>2</sub> must be present in excess; T. 170-350° and 225-275°; pressure slightly in excess of 1-2 atm.; higher pressures without essential effect.	Ni, Fe, Co, Pt, Cu, Cr, Mn, T, Mo, V, W, W-Th; the contact zones are placed in liquid baths, the liquid outside the baths cooled, <i>e.g.</i> , by using them for preheating or vaporizing of olefin polymers to be hydrogenated.	International Hydrogenation Patents Co., Ltd.: F.P. 809,351, March 2, 1937.
Hydrogenation of diisobutylene to isooctane; if the hydrogenation charge contains catalyst poisons, it is led over a hydrogenation catalyst until its activity decreases 5 to 30%; when poison-free, it is led over the catalyst until it regains complete activity and then is recharged with poison-containing hydrogenation charge; if the hydrogenation charge is free from poisons, a poison-containing hydrogenation gas (S) may be used, and in the regeneration period it is worked with the poison-free hydrogenation gas.	Usual hydrogenation catalysts.	International Hydrogenation Patents Co., Ltd. (Taylor): E.P. 465,024, May 27, 1937.

Table 7. Catalytic Hydrogenation of Unsaturated Organic Compounds.

Reaction	Catalyst	Observer
Hydrogenation of unsaturated organic cpds.	Pd black.	Gregem: (1866).
Hydrogenation of unsaturated organic cpds.	Pt, Pd, Rh; Ni, Co, Fe, Cu.  Pt black, colloidal Ni.	Bredig: "Anorganische Fermente," Leipzig, 1901. Bredig, Müller and Berneck: <i>Z. physik. Chem.</i> , 31, 258 (1899).
Hydrogenation of unsaturated organic cpds.	Action of oxides, such as ZnO-Cr <sub>2</sub> O <sub>3</sub> .	
Hydrogenation of unsaturated organic cpds.	PdCl <sub>2</sub> and a protective colloid, such as gum arabic.	G.P. 230,724, Kl 12o, Gr 27, April 29, 1909.
Hydrogenation of unsaturated organic cpds.	Ni-Pd on alumina or pumice.	Lessing: Austrian P. 82,207, Dec. 27, 1920.

Table 7 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of unsaturated organic cpds.	Pt, Ni, Cu, Ag.	Sandonini: <i>Gazz. chim. ital.</i> , <b>52</b> (1), 394-408 (1922).
Hydrogenation of unsaturated organic cpds.	Metal catalysts.	Sabatier: <i>Ind. Eng. Chem.</i> , <b>18</b> , 1005-1008 (1926).
Hydrogenation of unsaturated organic cpds.	Reduced Cu.	Komatsu and Kureta: <i>Mem. Coll. Sci., Kyoto Imp. Univ. (A)</i> , <b>II</b> , 163-169 (1927).
Hydrogenation of ethers from acids in the presence of H <sub>2</sub> into primary alcohols; T. 250°; pressure, 220 atm.; yield, 80-98%.	A chromite obtained by heating a mixture of Cu and a Zn chromate.	Adkins and Connor: <i>J. Am. Chem. Soc.</i> , <b>53</b> , 1091 (1931).
Hydrogenation of all ordinary types of unsaturated linkages; simple unsaturated C—C linkages, such as ethylene, not hydrogenated.	Ni or Cu chromite. Zn chromite.	Adkins and Connor: <i>Ibid.</i> , <b>53</b> , 1091 (1931). Vaughen: <i>Ibid.</i> , <b>53</b> , 3719 (1931).
Hydrogenation of unsaturated organic cpds.; elevated temp. and pressure.	A chromite obtained by calcining a mixture of a 6-valent Cr cpd. and a metal cpd. at red heat; treatment with a dilute acid promotes hydrogenation.	Canadian Industries, Ltd. (Lazier): Can. P. 323,471, June 21, 1932.
Hydrogenation of unsaturated organic cpds.		Farmer and Galley: <i>J. Chem. Soc.</i> , <b>1933</b> , 687-96.
Hydrogenation of unsaturated hydrocarbon mixtures: <i>n</i> -octane into octane; T. 300°; pressure, 135 atm. H <sub>2</sub> ; c.p. 777: 125-126 5°; $n_D^{20} = 1.3979$ ; $D_4^{20} = 0.7030$ .	Traces of a catalyst from previous experiments.	
Preparation of aromatic hydrocarbons from gaseous olefins; T. 300-500°; pressure 40 atm.; a liquid polymer is obtained which is led over H <sub>2</sub> ; under high pressure, aromatic hydrocarbons are obtained.	Active charcoal or silica gel; Ca molybdate; Fe filings; MoO <sub>3</sub> , Cr <sub>2</sub> O <sub>3</sub> .	I. G. Farbenindustrie A.-G. (Wietzel and Pfandler): U.S.P. 1,910,910, May 23, 1933.
Hydrogenation of olefins at 100-300° especially within 150-250° and under high pressure, 10 to 50 atm., in the presence of basic substances, such as alkali hydroxides, Ca or Mg oxide; 1 vol. C <sub>2</sub> H <sub>4</sub> , 2 vol. H <sub>2</sub> O vapor, 30 atm. pressure led over pumice impregnated with NaOH at 200°; water and aliphatic alcohols condensed from reaction mixture; a mixture of equal volumes of C <sub>2</sub> H <sub>4</sub> and H <sub>2</sub> O in 50% KOH introduced at 150° under 20 atm. pressure; successful without water; alcohols formed.	Basic substances in a solid state, such as wood; charcoal, asbestos, pumice, or active silica; also additions of Th oxide. Pt, Au, Ag, Cu with or without compounds of these metals.	Dreyfus: E.P. 389,136, April 6, 1933.
Hydrogenation of organic halide derivatives in alkaline solutions to counteract the poisoning effect of the hydrogen halide; in an alkaline medium, hydrogenation proceeds faster than in a neutral medium.	Pd charcoal (20 g. medicinal C Merck, Fe-free, introduced into a solution of 2 g. PdCl <sub>2</sub> in 570 cc. H <sub>2</sub> O + 2.6 cc. conc. HCl, which is heated on a water bath, decanted, washed with H <sub>2</sub> O until chlorine free and dried over NaOH).	Mladenovic: <i>Bull. soc. chim. roy. Yougoslav.</i> , <b>4</b> , 187-196 (1933).
Hydrogenation of unsaturated organic cpds.; T. 300-500°; a reaction under self-developing pressure.	Zn and H <sub>2</sub> O added to the hydrocarbons; ZnO formed (may be reduced through hydrocarbons and the Zn powder used again).	Pförmann: Can. P. 344,041, Aug. 21, 1934.
Hydrogenation of unsaturated $\alpha$ -keto acids, aldehydes and alcohols.	Fermented yeast.	Fischer and Wiedemann: <i>Ann.</i> , <b>513</b> , 260-280 (1934).



Table 7 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of olefins; T. greater than 100°; elevated pressure; the container is made of a metal the normal electrode potential of which lies between +0.2-0.4, such as Cu and Cu alloys with Cu predominant, and related to a scale at which the normal electrode potential of hydrogen is zero.	Aqueous H <sub>2</sub> SO <sub>4</sub> and sulfates of Be, Mg, Zn, Cd, Al, Mn, Cr, Co, Ni.	N. V. de Bataafsche Petroleum Mij.; P.P. 786,687, Sept. 7, 1935.
Hydrogenation of unsaturated organic cpds. under pressure.	Cr <sub>2</sub> O <sub>3</sub> heated in a stream of H <sub>2</sub> stepwise: (1) 150°; (2) 350° and (3) 410-440°.	Pokorski and Moldawski; Russ. P. 48,206, Aug. 31, 1936.
Hydrogenation of unsaturated hydrocarbon mixtures, e.g., allyl alcohol and oleic acid; the addition of allyl alcohol retards from the beginning the reduction of oleic acid until complete reduction (10-30 min.) of alcohol takes place, when the reduction of oleic acid proceeds with decreased velocity; both components are hydrogenated separately and the selectivity of the catalyst action is strongly expressed; allyl alcohol addition expresses the action of a catalyst poison.	Pt black (prepared according to Willstätter from H <sub>2</sub> PtCl <sub>4</sub> with CH <sub>2</sub> O in an alkaline medium).	Bogdanow and Baschkirowa; <i>Izvest. Akad. Nauk U.S.S.R.</i> , 91-108 and 109-21 (1936).
Hydrogenation of unsaturated organic cpds. (a method to determine unsaturated cpds. in benzene).	Prepared from an aqueous solution of PtCl <sub>2</sub> with gum arabic as a protective colloid and the addition of a small amount of Pd; 0.05 g. PtCl <sub>2</sub> in 3 cc. H <sub>2</sub> O + 0.05 g. gum arabic in 3 cc. H <sub>2</sub> O + 3 drops of colloidal Pd; shaken in a burette up to a constant H <sub>2</sub> volume.	Dobrotworskaja; <i>Khim. Tverdogo Topliva</i> , 8, 375-384 (1937).
Hydrogenation of unsaturated hydrocarbons; T. 200°.	Cr <sub>2</sub> O <sub>3</sub> stabilized with difficultly reducible oxides: Al, Zr, Ti, Si, Th, B, or Mg (5%) and readily reducible oxides of Te, Be, Pb, or Hg (0.5-5.0%).	Phillips Petroleum Co. (Frey and Huppke); U.S.P. 2,098,960, Nov. 16, 1937.
Hydrogenation of olefins with H <i>in statu nascendi</i> to paraffins; 6.4 mol diisobutylene gives a gaseous product consisting of paraffin and aromatic hydrocarbons (35%); (no unsaturated hydrocarbons) and consists of H and hydrocarbons of the CH <sub>4</sub> series; T. 400° (in an autoclave); initial pressure, 50 atm. H <sub>2</sub> corresponding to 5.6 mol H causing 70% hydrogenation; hydrogenation mechanism explained by secondary affinity of H <sub>2</sub> to the double bond in P <sub>2</sub> O <sub>5</sub> , whereby P changes into the three valent form:	P <sub>2</sub> O <sub>5</sub> , lampblack (P <sub>2</sub> O <sub>5</sub> is believed to be activated through olefins and other unsaturated hydrocarbons).	Malishev; <i>Oel, Kohle, Erdoel, Teer</i> ; 479-483 (1938).
$\begin{array}{c} \text{O} \\ \parallel \\ \text{O}=\text{P}-\text{O}-\text{P}=\text{O} \end{array} + \text{H}_2 \rightarrow \begin{array}{c} \text{O} \\ \parallel \\ \text{O}=\text{P}-\text{O}-\text{P} \begin{array}{l} \nearrow \text{O} \text{H} \\ \searrow \text{O} \text{H} \end{array} \end{array}$		
The mechanism of catalysis with P <sub>2</sub> O <sub>5</sub> is different from that with H <sub>3</sub> PO <sub>4</sub> .		
Hydrogenation of olefin polymers.	Obtained by heating Ni formate with light olefin polymers to 100-250° under pressure whereby the olefin polymers evaporate.	Shell Development Co. (Williams and McAllister); Can. P. 373,994, May 24, 1938.

Table 7 (Continued).

Reaction	Catalyst	Observer
Selective hydrogenation of olefins together with aromatics, for example, hydrogenation of benzene with addition of amylene proceeds 50% slower than alone, while toluene (difficult to hydrogenate alone) when substituted with amylene (1 : 1) is completely hydrogenated in 6 hrs. at 40°; hydrogenation of xylene is promoted by amylene; in mixtures of diisobutylene and benzene and toluene respectively, hydrogenation of diisobutylene only takes place; this was ascertained for diisobutylene and toluene, also for a continuous hydrogenation at 115-175°; octadecene is hydrogenated in the presence of benzene at 23, 50, 75, 100 and 150° without marked hydrogenation of benzene taking place; hydrogenation of amylene in the presence of toluene and <i>n</i> -heptane (15 : 15 : 70) without associated hydrogenation of toluene takes place at 22° in 6 hours.	Ni obtained by precipitation of NiSO <sub>4</sub> in the presence of kieselguhr with Na <sub>2</sub> CO <sub>3</sub> and reduction of the obtained basic Ni carbonate.	Ipatieff and Corson; <i>Ind. Eng. Chem.</i> , 30, 1039-1040 (1938).
Hydrogenation of olefinic hydrocarbons to saturated hydrocarbons; especially polymerization products of gaseous olefins; T. 175-315°; pressure up to 35 atms. in two steps: (1) so much H <sub>2</sub> is added that only partial hydrogenation follows; (2) the hydrogenation is then perfected with addition of fresh H <sub>2</sub> ; products consist of 98% saturated hydrocarbons and represent antiknock motor propellants.	Usual catalysts.	Universal Oil Products Co. (Pyzel): U.S.P. 2,138,881, Dec. 6, 1938.
Hydrogenation of unsaturated ethers or esters by H <sub>2</sub> ; T. less than 200°; these cpds. contain at least one olefinic bond between two aliphatic C atoms, of which one is a tertiary C atom which may stand near the ether group and one or more ether or ester groups; examples of initial substances:	Active hydrogenation catalyst.	Shell Development Co. (Groll and Burgin): U.S.P. 2,122,812, July 5, 1938. Can. P. 375,525, Aug. 2, 1938.
$\text{CH}_2=\text{C}(\text{CH}_3) \cdot \text{CH}_2-\text{O}-\text{CH}_3 \rightarrow \text{CH}_2=\text{C}(\text{CH}_3) \cdot \text{CH}_2-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$ $\text{CH}_3\text{COOCH}_2 \cdot \underset{\text{CH}_3}{\text{C}}-\text{CH}_2-\text{O}-\text{CH}_3 \rightarrow \text{C}_6\text{H}_5-\text{CH}=\text{C}(\text{CH}_3) \cdot \text{CH}_2-\text{O}-\text{CH}_3$ $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}_2-\text{CH}_2 \\ \diagdown \\ \text{CH}_2-\text{C}=\text{CH}-\text{CH}_2-\text{O}-\text{CH}_3 \end{array} \rightarrow \begin{array}{l} \text{CH}_2=\text{C}(\text{CH}_3) \cdot \text{CH}_2-\text{OOC} \cdot \text{CH}_3 \\ \text{CH}_2=\text{C}(\text{CH}_3) \cdot \text{CH}_2-\text{OOC} \cdot \text{COOH} \end{array}$ $\text{CH}_2=\text{C}(\text{CH}_3) \cdot \text{CH}_2-\text{OOC}-\text{COO} \cdot \text{CH}_3 \rightarrow \text{CH}_3 \cdot \text{COO}-\text{CH}_2-\underset{\text{CH}_3}{\text{C}}-\text{CH}_2\text{OH}$		
Hydrogenation of unsaturated organic cpds., e.g., abietyl cpds. with hydrogen (at 100-210° and 1000-5000 lbs./sq.in.) in liquid phase and in opposite stream.	An alloy of Al, Ni, and a metal from the group of Cu, Zr, Ce, and Co.	Hercules Powder Co. (Byrkit, Jr.): Can. P. 378,273, Dec. 13, 1938.
Hydrogenation of olefin polymers to saturated hydrocarbons of high antiknock value.	Mixed catalysts from sulfides of Mo and W as well as sulfides of Ni, Co, Ag, or Cu, whereby the sulfides of Mo and W must be present in a smaller amount than the others.	N. V. Internationale Maatschappij voor Hydroerings-Techniek and Chemie: Ind. P. 25,333, Jan. 21, 1939.

Table 8. Catalytic Hydrogenation of Cyclic and Heterocyclic Compounds.

Reaction	Catalyst	Observer
Hydrogenation of cyclic hydrocarbons to tetranaphthalene.	Na, NH <sub>3</sub> .	Lebeau and Pieon: <i>Compt. rend.</i> , <b>158</b> , 1514-1517 (1912); <b>159</b> , 70-72 (1913).
Hydrogenation of cyclic cpds. under pressure.	Os.	Ssadikow and Michailow: <i>J. Chem. Soc.</i> , <b>1928</b> , 438-448.
Hydrogenation of bicyclohexylmethane to cyclohexone; pressure not less than 70 atm.	Fe-alumina.	Ipatieff, Orloff and Lichatschew: <i>Ber.</i> , <b>63</b> , 156 (1930).
Hydrogenation of cyclohexylidene-cyclohexanone to cyclohexyl-cyclohexanone and its homologs; a mixture of isomers methylcyclohexyl and methylcyclohexanol (c.p. 265-280°) obtained; T. 150°; pressure increases up to 10 atm.	Non-noble metals, e.g., Ni catalyst with MgO as a promoter; Fe and Cu or their mixtures may be used as promoters; MgO, Cr <sub>2</sub> O <sub>3</sub> .	Howards and Sons, Ltd. (Blagden and Clark): E.P. 397,883, Sept. 28, 1933.
Hydrogenation of simple homologs of cyclopentane: methylcyclopentane and ethylcyclopentane formed by hydrogenation of a mixture of hydrocarbons which, on account of the c.p. are not complex; the reaction involves the splitting of the 5-ring propylcyclopentane, accompanied by a complex decomposition resulting in the formation of low molecular weight hydrocarbons.	Pt charcoal, 305-315°.	Zelinsky, Kasansky and Plates: <i>Ber.</i> , <b>68</b> , 1869-1872 (1935).
Hydrogenation of heterocyclic compounds: indol to 2,3-dihydroindol; T. 150-250°; pressure, ordinary or elevated.	Cu carbonate and alumina hydrate precipitated with Na bicarbonate solution; Cu-silica gel.	I. G. Farbenindustrie A.-G.: G.P. 623,693 (1934).
Hydrogenation of 2-methyl-bicyclo-(1,2,2)-heptene; T. 125-130°; with excess H <sub>2</sub> , gives the same reaction product as in the liquid phase; catalytic conversion of 2-methyl-bicyclo-(1,2,2)-heptene-5 forms at 300° in N <sub>2</sub> , with poisoning of the catalyst, a high molecular weight product, while 2-methyl-bicyclo-(1,2,2)-heptane over the same catalyst converts at 300-310° into cyclopentane, paraffins and a little <i>m</i> -xylene.	Platinized charcoal.  Pt charcoal.	Kasanski and Tschernowa: <i>Zhur. Obschei Khim.</i> , <b>8</b> (70), 651-653 (1938).

Table 9. Catalytic Hydrogenation of Acetylene.

Reaction	Catalyst	Observer
Hydrogenation of C <sub>2</sub> H <sub>2</sub> to C <sub>2</sub> H <sub>4</sub> ; T. 100°; yield, 90%.	Pt metal group mixed with a base metal; Ni : Pd = 10 : 1 on charcoal or ton.	Caro and Frank: G.P. 339,493, Kl 12o, Gr 1, July 27, 1921.
Hydrogenation of C <sub>2</sub> H <sub>2</sub> in liquid phase; T. 700°; yield, 40.5%.	Active charcoal.	Zelinsky: <i>Ber.</i> , <b>57</b> , 264 (1924).
Hydrogenation of C <sub>2</sub> H <sub>2</sub> to C <sub>2</sub> H <sub>4</sub> .	Pd on silicic acid gel.	Morris and Reyerson: <i>J. Phys. Chem.</i> , <b>31</b> , 1332 (1927).
Hydrogenation of C <sub>2</sub> H <sub>2</sub> to C <sub>2</sub> H <sub>4</sub> exclusively.	Pt on silicic acid gel.	
Hydrogenation of C <sub>2</sub> H <sub>2</sub> to C <sub>2</sub> H <sub>4</sub> in the presence of water vapor (5-10%).	Ni, Co, Cu, Pd or Cr on kieselguhr.	I. G. Farbenindustrie A.-G.: F.P. 688,791 (1930). E.P. 325,152 (1930).
Hydrogenation of C <sub>2</sub> H <sub>2</sub> to C <sub>2</sub> H <sub>4</sub> ; T. 180-500°; optional pressure.	Te on kieselguhr or active charcoal.	I. G. Farbenindustrie A.-G.: E.P. 336,999 (1930).
Hydrogenation of C <sub>2</sub> H <sub>2</sub> in paraffin oil; T. 80-100°; reaction begins at room temp.; C <sub>2</sub> H <sub>2</sub> : H <sub>2</sub> = 1 : 2; T. 200°; yield, 80%.	Ni-kieselguhr activated by ThO <sub>2</sub> or Al <sub>2</sub> O <sub>3</sub> .	Fischer and Peters: <i>Brennstoff-Chem.</i> , <b>12</b> , 286 (1931).
Hydrogenation of C <sub>2</sub> H <sub>2</sub> .	Pt (colloidal Pd).	

Table 9 (Continued).

Reaction	Catalyst	Observer
	Pt black.	Lebedew and Stern; <i>Zhur. Obshchei Khim.</i> , 2, 249-259 (1932).
Hydrogenation of $C_2H_2$ to $C_2H_4$ ; yield, 90%.	Ni or Pd on kieselguhr; Ni alone catalyzes to $C_2H_4$ .	Joshikawa; <i>Bull. Chem. Soc. Japan</i> , 7, 201 (1932).
Hydrogenation of $C_2H_2$ .		Salkind and Teterin; <i>Ber.</i> , 66, 321-325 (1933). Salkind, Wischujakow and Morew; <i>Zhur. Obshchei Khim.</i> , 3 (65), 91-113 (1933).
Hydrogenation of $C_2H_2$ in liquid phase; $C_2H_2:H_2=1:5$ ; T. $170^\circ$ ; pressure, 25 atm.; yield, 70% liquid products.	Active charcoal-Cu suboxide.	Kwal; <i>Chimie &amp; industrie</i> , 34, 773 (1935).
Hydrogenation of $C_2H_2$ . $C_2H_2$ , $C_2H_4$ ; T. $-78^\circ$ ; pressure, 0.05 mm. Hg; the desorption of $H_2$ and reaction velocity are followed by measurements of electric resistance of Pd layer; velocity of desorption is always smaller because the potential barrier for the reaction of $C_2H_2$ with adsorbed $H_2$ is smaller than for desorption; hydrogenation velocity is limited by supply velocity of $H_2$ to the surface, or by velocity of a surface process; the dependence on supply velocity may be ascertained by investigation of reaction velocity depending upon conc. of the dissolved $H_2$ .	Pd ( $H_2$ dissolved in it).	Dobytschin and Frost; <i>Acta Physicochim. U.R.S.S.</i> , 5, 111-130 (1936). Dobytschin and Frost; <i>Zhur. Fiz. Khim.</i> , 7, 742-753 (1936).
Hydrogenation of $C_2H_2$ to $C_2H_4$ ; resistance measurements serve to find velocity of charge by hydrogen and discharge by acetylene and $C_2H_2$ ; the charging velocity is found to be proportional to $H_2$ pressure ( $H_2$ pressure between 36 and 720 mm. Hg); the discharge velocity of $C_2H_2$ and $C_2H_4$ ( $H_2$ pressure between 30 and 720 mm. Hg) depends on pressure in the case of $C_2H_2$ and not in the case of $C_2H_4$ ; $C_2H_2$ is adsorbed more strongly than $C_2H_4$ by Pd containing $H_2$ ; discharge process is in accordance with the equation:	Pd wire (subjected to activation by anodic polarization).	
$d(2H/dt) + a(dH/dt) + b = 0$ , where $dH/dt$ = time decrease of H adsorbed by Pd; inhibition increases linearly with the substance exchange caused by the discharge.		
Hydrogenation of $C_2H_2$ to $C_2H_4$ in excess $H_2$ ; 70% $C_2H_2$ converted into $C_2H_4$ ; in addition to $C_2H_4$ , liquid polymerization products are formed; $C_2H_4$ formation retarded by the use of narrow tubes, and the polymerization hindered by using short catalyst layers.	Ni-kieselguhr.	Ackermann; <i>Brennstoff-Chem.</i> , 18, 357-361 (1937).
Hydrogenation of $C_2H_2$ to $C_2H_4$ .	Pd-silica gel.	
Hydrogenation of $C_2H_2$ .	Fe (above $180^\circ$ ).	
Hydrogenation of $C_2H_2$ to $C_2H_4$ .	Silica gel covered with Pt or Cu metal.	
Hydrogenation of $C_2H_2$ .	Fe-Cu alkali.	
Hydrogenation of $C_2H_2$ to $C_2H_4$ .	Al powder; Ce or Ce oxide mixed with active charcoal, asbestos or kieselguhr.	

Table 9 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of $C_2H_2$ .	$Cu(C_2H_5)_2$ —cuprene formed.	
Hydrogenation of $C_2H_2$ to $C_2H_4$ or $C_2H_6$ .	Reduced Co entirely free from Ni (T. $180^\circ$ ).	
Hydrogenation of monovinyl acetylene to a mixture of butadiene and butylene; ratio of butadiene to butylene = 77 : 23.	Ni, Pd, Pt, or Co on ton or pumice; Pd on ton.	I. G. Farbenindustrie A.-G.: F.P. 828,194, May 11, 1938. F.P. 828,195, May 11, 1938.
Semi-hydrogenation of acetylene derivatives; hydrogenation of acetylene is impossible in the cold; on the contrary, heptene-1, octene-1 phenyl acetylene, 1-methoxyoctene-2, and 3-methoxyphenyl-1-propyne-1 are converted at $100$ – $110^\circ$ under 40–50 atm. into the corresponding ethylene derivatives; the hydrogenation velocity is constant up to adsorption of one mol $H_2$ per acetylene bond; with pure methyl noninate the same results are obtained, while with the commercial product contradictory results were obtained.	Ni obtained from a Ni-Al alloy (refer to C. 1937 I 1907); active Fe (black, strong pyrophoric powder) obtained from $FeAl_3$ by treatment with NaOH solution (by contacting $C_6H_5NO_2$ the active Fe is strongly heated and partial conversion into azobenzene is effected); suitable for catalyzing; conversion of triple bonds into double bonds by specific hydrogenation; double bond not affected by this catalyst.	Paul and Hilly: <i>Compt. rend.</i> , <b>206</b> , 608–10 (1938).

Table 10. Catalytic Hydrogenation of Methyl Alcohol.

Reaction	Catalyst	Observer
Hydrogenation of $CH_3OH$ .	$Ni(CO)_4$ + 0.05–0.3% by volume $O_2$ .	Sabatier and Senderens: <i>Compt. rend.</i> , <b>137</b> , 301 (1903).
Hydrogenation of $CH_3OH$ at high temp. and pressure; in this process part of the $CH_3OH$ actually remains undecomposed, indicating that the reaction was reversible (1) $CH_3OH \rightarrow HCHO + H_2$ (2) $HCHO \rightarrow H_2 + CO$ (3) $CO + 3H_2 \rightarrow CH_4 + H_2O$ (4) $CH_3OH + H_2 \rightarrow CH_4 + H_2O$ (5) $CH_4 + 4H_2O \rightarrow CO_2 + 6H_2 + O_2$	Reduced Ni.	Ipatieff: <i>J. prakt. Chem.</i> , <b>87</b> , 479 (1912).
Hydrogenation of $CH_3OH$ .	Ni, Cu.	Elektrizitätswerke Lonza A.-G.: G.P. 317,589 (1918). Swiss P. 74,129 (1916). Armstrong and Hilditch: <i>Proc. Roy. Soc. London (A)</i> , <b>97</b> , 259 (1920). Badische Anilin- und Soda Fabrik: G.P. 350,048 (1921). E.P. 158,906 (1921).

Table 11. Catalytic Hydrogenation of Ethyl Alcohol.

Reaction	Catalyst	Observer
Hydrogenation of $\delta$ -phenylethyl alcohol or its derivatives to esters of acetic acid.	Pt, Pd, Ni.	Packendorf: Russ. P. 44,927, Nov. 30, 1935.
Hydrogenation of w-acetoxyacetophenone or nucleus substitutes; 20 parts w-acetoxyacetophenone dissolved in 50 parts alcohol in the cold; normal $H_2$ pressure; quantitative yield.	0.5 part 10% Pt.	

Table 12. Catalytic Hydrogenation of Various Alcohols.

Reaction	Catalyst	Observer
Hydrogenation of organic compounds, such as crude alcohol mixture obtained in catalytic dehydrogenation of alcohol under pressure consisting of butanol, unsaturated com-	Chromate catalysts consisting of a double chromate of a N cpd. ( $NH_3$ , aniline, methylamine, pyridine) and a metal acting as a hydrogenation catalyst: Fe, Ni, Co, Cu, Sn, heat-	Dupont (Lazier): U.S.P. 1,964,000, June 26, 1934.

Table 12 (Continued).

Reaction	Catalyst	Observer
pounds such as crotonyl alcohol, esters, and the like; T. 120-170°; time, 30 min.; pressure, 200 atm.; iodine number drops from 100 to 3.	ing them to 200-400°; reduced at 400-600°; best at 500°; 17,650 g. Ni(NO <sub>3</sub> ) <sub>2</sub> dissolved in 3 l. of water mixed with a solution of 750 g. NH <sub>4</sub> bichromate in equal parts of water, and the solution heated to 90-100° for 30 min. with stirring; double chromate of NH <sub>4</sub> and red Ni ppt. is washed, dried at 400°; reduced for 12 hours in a stream of dry H <sub>2</sub> .	
Hydrogenation of wood spirit to methyl alcohol in a treated* liquid phase; T. 100-150°; time, 2-3 hrs.; pressure, 60 atm. *T. less than 300°.	Hydrogenation catalysts.	Deutsche Hydrierwerke A.-G. (Schrauth): G.P. 619,438, Kl 12o, Oct. 17, 1935.
Hydrogenation of high molecular polyvalent alcohols to low molecular polyvalent alcohols; T. 200°; high pressure, 1000 lbs. per sq. in.	Co, Ni containing a weak basic cpd. such as alkaline-earth carbonate, borax, Al(OH) <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> ; for Ni or Co may be substituted Ni chromite or Cu-Zn cpds.	Dupont (Rothrock): U.S.P. 2,004,135, June 11, 1935.
Hydrogenation of butanol-1 and -3; in aqueous solution: in gaseous phase:	Ni. Cu on pumice.	Consortium für Elektrochemische Industrie G.m.b.H.: E.P. 494,391, Nov. 24, 1938. F.P. 834,557, Nov. 24, 1938.

Table 13. Catalytic Hydrogenation of Crotonic Aldehyde.

Reaction	Catalyst	Observer
Hydrogenation of crotonic aldehyde with H <sub>2</sub> to butyl alcohol.	Cu; Ni in the presence of H <sub>2</sub> O.	Badische Anilin- und Soda Fabrik: G.P. 407,837 (1922). Chemische Fabrik Griesheim Elektron A.-G. (Grunstein): F.P. 518,240 (1920).
Hydrogenation of crotonic aldehyde with H <sub>2</sub> to butyraldehyde.	Cu + water glass; Cu + Ni in the presence of H <sub>2</sub> O.	Badische Anilin- und Soda Fabrik: G.P. 362,537 (1921). Chemische Fabrik Griesheim Elektron A.-G. (Grunstein): B.P. 147,118 (1920).
Hydrogenation of crotonic aldehyde; T. 90°; pressure, 10 atm.; time, 1½ hr. yield, 87% n-butyraldehyde, 3% crotonic aldehyde (both liquid products) and 6% condensation products.	Ni-kieselguhr.	Konsortium für Elektrochemische Industrie (Mugdon and Wimmer): U.S.P. 1,730,587 (1930).
Hydrogenation of crotonic aldehyde.	Na chromate and Ni sulfate react, forming basic Ni chromate containing a little Na chromate; ppt. washed, dried and heated to a weak red glow, and the cooled black mass extracted with hot water and reduced with H <sub>2</sub> .	Dupont (Lazier): U.S.P. 2,077,421, April 20, 1937.
Hydrogenation of crotonic aldehyde.	Raney's low-temp. hydrogenating catalyst not suitable for large-scale work; Ni prepared by precipitation of NiSO <sub>4</sub> with Na <sub>2</sub> CO <sub>3</sub> ; the Na <sub>2</sub> SO <sub>4</sub> formed is removed with difficulty because the NiCO <sub>3</sub> is not washed on the filter; rather, water is added while stirring and the precipitate filtered after each addition; complete removal of Na <sub>2</sub> SO <sub>4</sub> is therefore impossible; after the sixth washing, the catalyst has optimum activity; to establish an equilibrium between the amount of salt adsorbed and the wash water in large-scale operation, the ppt. is ground in a colloid mill.	Sully: <i>Chimie &amp; industrie</i> , 58, 282-84 (April 4, 1939).

Table 14. Catalytic Hydrogenation of Various Aldehydes.

Reaction	Catalyst	Observer
Hydrogenation of benzaldehyde.	Fe.	Ipatieff: <i>Ber.</i> , <b>41</b> , 993 (1908).
Hydrogenation of various aldehydes to alcohols.	Pt oxide.	Carothers and Adams: <i>J. Am. Chem. Soc.</i> , <b>46</b> , 1675-1683 (1924).
Hydrogenation of cinnamic aldehyde to hydrocinnamic aldehyde.	Ni(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O on kieselguhr (precipitated at 70-80°, dried at 110-120° and reduced with dry H <sub>2</sub> at 450°).	Adkins and Cramer: <i>J. Am. Chem. Soc.</i> , <b>52</b> , 4349 (1930).
Hydrogenation of HCHO (a certain amount of acid is formed as a result of Cannizzaro's reaction); yield, 50%; duration of reaction, 30 hrs.; NaOH (0.5N) $2\text{HCHO} + \text{NaOH} \rightarrow \text{CH}_3\text{OH} + \text{NaCHO}_2$	4.5 g. Raney's Ni.	Delépine and Horeau: <i>Compt. rend.</i> , <b>204</b> , 1605-1608 (1937).
Hydrogenation of HCHO (3 g. HCHO dissolved in 100 cc. 0.5N NaOH); reaction completed in 70 min.; yield, after 30 min., 97%.	4.5 g. Raney's Ni.	
Hydrogenation of: (1) crotonic aldehyde to butyraldehyde and butyl alcohol; (2) isopulegol to menthol.	Ni obtained by precipitating an aqueous solution of a Ni salt by an alkali carbonate, washing the alkali salt, drying and reducing the ppt. to metallic Ni and then suspending it in a sulfur-free mineral oil (c.p. greater than 300°) or any other inert liquid; also, mixed catalysts may be prepared, e.g., Ni and Cu, or Al and Mg; catalyst regenerated with dry or superheated water vapor and refreshed with H <sub>2</sub> or a gas acting similarly.	Durrans and Sully: E.P. 478,386 (1938). E.P. 478,487, Feb. 17, 1938.
Hydrogenation of aliphatic aldehydes (in vapor phase) with H <sub>2</sub> , NH <sub>3</sub> and primary aliphatic amines at high temp. to secondary and tertiary aliphatic amines; e.g., 10.5 g. monoethylamine in 43 g. of a 70% by volume H <sub>2</sub> and 30% by volume NH <sub>3</sub> mixture are evaporated on one hand and 24 g. acetaldehyde in 1 g. H <sub>2</sub> on the other; both gas streams are united and led at 130° over 100 g. of Ni catalyst; the aldehyde changes into an 85-90% amine mixture which consists of 84% diethylamine and 16% triethylamine; likewise di- and tri-butylamine are prepared from monobutylamine and butyraldehyde.	Hydrogenation catalysts; Ni.	I. G. Farbenindustrie A.-G. (Christ): G.P. 671,839, Kl 12g, Feb. 14, 1939; add to G.P. 489,551; (Refer to C. 1931 I 1823)

Table 15. Catalytic Hydrogenation of Ketones.

Reaction	Catalyst	Observer
Hydrogenation of acetone to pinacone; yield especially good in the presence of HgCl <sub>2</sub> .	Al or Mg amalgam; alkali.	G.P. 233,894, Kl 12o, Gr 5, June 3, 1910. G.P. 241,896, Kl 12o, Gr 5, 1910.
Hydrogenation of a ketone (photochemical reduction).	Yeast.	Neuberg and Lewite: <i>Biochem. Z.</i> , <b>91</b> , 251-266, Oct. 31, 1918.
Hydrogenation of acetone to formic acid.	Zr, Cu, Ni, alumina, ThO <sub>2</sub> , Mo.	Maihle and deGodow: <i>Compt. rend.</i> , <b>152</b> , 1212 (1911). Maihle and deGodow: <i>Bull. soc. chim.</i> , <b>4</b> (2), 61-64 (1911).
Hydrogenation of acetophenone; T. 350°.	Cu.	Sabatier and Kubote: <i>Compt. rend.</i> , <b>172</b> , 733-736 (1921).
Hydrogenation of pulegone to menthone.	Pd or <i>p</i> -xylidine.	Skita: <i>Ber.</i> , <b>55</b> , 139-143 (1922).

Table 15 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of ketones.	Pt black (pure and containing Fe).	Faillotin: <i>Compt. rend.</i> , <b>182</b> , 138-140 (1926).
Hydrogenation of dibenzalacetone under pressure.		Ipatieff and Orlov: <i>Compt. rend.</i> , <b>184</b> , 751 (1927).
Hydrogenation of acetone to isopropyl alcohol.	NiO more effective than reduced Ni.	Ipatieff
Hydrogenation of benzophenone; synthesis of benzoyl chloride with benzene by means of the Friedel and Crafts reaction.	Mixed catalysts: FeCl <sub>3</sub> -AlCl <sub>3</sub> .	Riddell and Noller: <i>J. Am. Chem. Soc.</i> , <b>52</b> , 4365-4369 (1930).
Hydrogenation of aldehyde and ketone derivatives: oximes derived from Me <sub>2</sub> CO, BuCHO, C <sub>6</sub> H <sub>5</sub> CHO and BzH (the oximes of Ph <sub>2</sub> CO and camphor were hydrogenated almost quantitatively to the corresponding amines); T. 100°; pressure, 100 atm. H <sub>2</sub> ; yield, 62-75% primary amines and 10-27% secondary amines.	Ni (for about one hour).	Winaus and Adkins: <i>J. Am. Chem. Soc.</i> , <b>55</b> , 2051-2080 (1933).
Hydrogenation of ethylidene acetone to methylpropyl ketone; T. 160°; pressure; 120 atm.	Ni-kieselguhr contact; Cu chromite; Cu-Ba chromite.	Morgan and Hardy: <i>J. Soc. Chem. Ind.</i> , <b>52</b> , 518-519 (1933).
Hydrogenation of acetophenone; T. 250°; (at 284-289°, the reaction stops completely).	Cu-ZnO-Cr <sub>2</sub> O <sub>3</sub> (precipitated from a nitrate solution with soda at 90°); weaker than Ni at ordinary pressure; explained by diminution of active surface as a result of reduction of ZnO to Zn and formation of an alloy between Zn and Cu.	Balassny: <i>Ukrain. Akad. Nauk, Zapiski Inst. Khim.</i> , <b>2</b> , 175-182 (1935).
Hydrogenation of 2.38 g. diphenyltriketone in benzene; T. 110-111.5°F.; pressure, 2.5 atm.	Pt-PtO <sub>2</sub> ; depending upon the amount of catalyst used, 1, 2, or 3 mols H <sub>2</sub> are adsorbed; for 0.05 g. PtO <sub>2</sub> , one mol H <sub>2</sub> is adsorbed.	Bigelow, Rule and Black: <i>J. Chem. Soc.</i> , <b>1935</b> , 83-85.
$\begin{array}{l} \text{(I) } \text{C}_6\text{H}_5\text{CO} \cdot \text{CO} \cdot \text{COC}_6\text{H}_5 \xrightarrow{\text{H}_2} \text{(II) } \text{C}_6\text{H}_5\text{COCH(OH)COC}_6\text{H}_5 \\ \text{diphenyltriketone.} \qquad \qquad \qquad \text{dibenzoyl carbinol.} \\ \qquad \qquad \qquad \text{C}_6\text{H}_5\text{CH(OH)CH(OH)CH(OH)C}_6\text{H}_5 \\ \qquad \qquad \qquad \downarrow \qquad \qquad \qquad \downarrow \\ \text{C}_6\text{H}_5\text{CH(OH)CO} \cdot \text{CH(OH)C}_6\text{H}_5 \rightleftharpoons \text{(III) } \text{C}_6\text{H}_5\text{CH(OH)CH(OH)COC}_6\text{H}_5 \\ \qquad \qquad \qquad \alpha, \gamma\text{-dioxo-}\gamma\text{-oxo-}\alpha, \gamma\text{-diphenylpropane} \end{array}$		
Hydrogenation of ketones in aqueous solution; only hydrogenation of the keto-group takes place.	Raney's Ni, as well as Pt-plated Raney's Ni, accelerated by adding alkali; Pt-plated Ni, as well as Pt black slowed down by adding alkali; Pt black has greater catalytic activity than Pt-plated Ni because the latter is not suitable for the hydrogenation of the aromatic nucleus; Pt black* poisoned by thiophene, and Raney's Ni gives like results.	Foresti and Chiummo: <i>Gazz. chim. ital.</i> , <b>67</b> , 408-416 (1937).
Hydrogenation of diketo-oximes and aceto-oximes in an acid medium to the corresponding diamines and NH <sub>4</sub> Cl: pentanone, heptanone, gaseous mixtures, particularly primary hydroxylamines.		Krajeinovic and Vranjican: <i>Bull. soc. chim.</i> , <b>53</b> , 145-150 (1933); <i>Chem. Abs.</i> , <b>22</b> , 2745.
Hydrogenation of ketones containing one or more carbonyl		Riedel A.-G.: <i>G.P.</i> 444,665, Kl 12o, Gr 25, May 27, 1927.

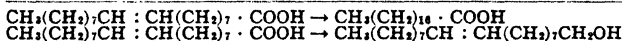


Table 16. Catalytic Hydrogenation of Fatty Acids.

Reaction	Catalyst	Observer
Hydrogenation of fatty acids.	Finely divided metals, especially Ni.	G.P. 141,029, Kl 23d, Aug. 14, 1902; (Refer to C. 1903 I 1199).
Hydrogenation of fatty acids (oleic).	Electric glow discharge.	G.P. 167,107, Kl 23b, March 30, 1904; (Refer to C. 1906 I 80).
Hydrogenation of fatty acids (oleic); T. 180°.	20% Ni on kieselguhr; SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Ce <sub>2</sub> O <sub>3</sub> on talc, wood charcoal, or bone charcoal; Zn, Pb, Ag, Sb on kieselguhr (Mg, Ca, Hg not active for hydrogenation).	Kailan and Stüber: <i>Monatsh.</i> , <b>62</b> , 90-100 (1932).
Hydrogenation of oleic to stearic acid in vapor phase.	Ni.	Sabatier and Maible: <i>Ann. chim.</i> ( <b>8</b> ), 16, 73 (1909).
Hydrogenation of fatty acids.	NiO.	Bedford and Erdmann: <i>J. prakt. Chem.</i> ( <b>2</b> ), <b>87</b> , 425-455 (1911). Bedford and Erdmann: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>45</b> , 616-643 (1913).
Hydrogenation of unsaturated fatty acids and their glycerides.	Ni borate.	Schonfeld: <i>Seifensieder-Ztg.</i> , <b>41</b> , 945-949 (1912). Badische Anilin- und Soda Fabrik: G.P. 362,143, Kl 12o, Oct. 23, 1921.
Hydrogenation of fatty acids.	Ni acetate.	Bremen Besingheimer Ölfabriken: G.P. 304,043, Kl 12g, Gr 2, Aug. 18, 1912.
Hydrogenation of unsaturated fatty acids.	Ni formate; Cu, Fe, or Co acetate, or the corresponding lactate.	Wimmer: G.P. 312,668, Kl 12o, May 28, 1919.
Hydrogenation of unsaturated fatty acids.	Ni + ton.	Feldenheimer and Plowman: E.P. 164,808 (1920).
Hydrogenation of fatty acids or fats.	Ni.	Berger: F.P. 517,898, May 14, 1921.
Hydrogenation of fatty acids.	NiCO <sub>3</sub> .	Maxted: <i>Chem. Age (London)</i> , <b>7</b> , 816-818 (1922).
Hydrogenation of fatty acids.	Ni soap.	Schicht and Grün: Austrian P. 90,481, Dec. 27, 1922.
Hydrogenation of fatty acids and their glycerides.	Cr and B to the exclusion of NiCO <sub>3</sub> .	Austrian P. 86,138, Nov. 10, 1921. Badische Anilin- und Soda Fabrik: G.P. 362,143, Kl 12o, Gr 27, Oct. 23, 1922.
Hydrogenation of oleic (32 g.) to stearic acid (62 g.) in vapor phase; T. 300°; activated H <sub>2</sub> instead of molecular H <sub>2</sub> used by Ni (addition of nascent H <sub>2</sub> follows).	Active charcoal.	Werschen-Weissenfelser Braunkohlen (Fürth and Hildebrandt): G.P. 441,164 (1926).
Hydrogenation (selective) of unsaturated fatty acids (a mixture of clupanodonic acid and the methyl ester of oleic acid).	0.1% Ni (under 60 atm. pressure); 0.5% Ni (at ordinary pressure); Ni under high pressure acts like Pt.	Ueno Junimori and Heda: <i>J. Soc. Chem. Ind. Japan</i> , <b>34</b> , 481B-483B (1931).
Hydrogenation of oleic or cinnamic acid (oleic hydrogenated as fast as cinnamic); T. 250-320°.	Ni on kieselguhr; (0.1 g. catalyst to 20 g. acid); Ni prepared by precipitation with Na <sub>2</sub> CO <sub>3</sub> ; the velocity of the process drops when Ni is prepared by precipitation with NaOH and still more when Ni-silicic acid is used.	Kailan and Hardt: <i>Monatsh.</i> , <b>58</b> , 307-368 (1931).

Table 16 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of 1 g. mol oleic acid to stearic acid (heat of hydrogenation, 53 cal.); heat set free in hydrogenation calculated from the combustion heat of unsaturated and saturated cmpds. by the following formula: $C_nH_{2n} + H_2 \rightarrow C_nH_{2n+2} + (69 + q - q_1)$		Terskich: <i>Masloboino Zhirovoe Delo</i> , 9 (3), 29-30 (1933).
Hydrogenation of oleic or cinnamic acid; the calculated unimolecular velocity constants pass through a maximum with increasing amounts of the catalyst; the maximum for 5-7 g. oleic acid substituted shows increasing conversion; for substituted amounts above 10 g., decreasing conversion; with cinnamic acid, increased conversion obtained almost throughout; in the case of oleic acid and olive oil, the constants increase almost proportionally to the square of the $H_2$ pressure; by increasing the hydrogenation temp. from 100° to 120°, the reaction velocity is doubled, after which it increases more slowly, reaching the maximum between 180-200°.	Ni; the amount of $H_2$ adsorbed by the catalyst increases with an increase in the catalytic activity; the constants of the alkyl esters of oleic and cinnamic acids having an even number of C atoms are greater than the constants of those having an uneven number of C atoms. Ni-kieselguhr (reduction temp. increases from 345° to 485° and then to 550°) increases the average value of $K_2 \cdot 10^4$ , obtained at 180° with optimum amount of catalyst and 10 g. oleic acid, from 646 to 1100 and then to 1300.	Kailan and Hartel: <i>Monatsh.</i> , 70, 329-373 (1937).
Hydrogenation of unsaturated fatty acids with at least eight C atoms, such as: oleic, linolenic, erucic acids, <i>et al.</i> , to higher unsaturated aliphatic alcohols; initial T. 100-200°; pressure, at least 30 atm.	Cu (containing 20-60% Cd with respect to the Cu content) precipitated on kieselguhr.	Bohme Fettchemie Gesellschaft: <i>F.P.</i> 819,255, Oct. 13, 1937.
Hydrogenation of ethylenic linkage in unsaturated fatty acids or their esters (the CO group remains unchanged);	Ni. Zn or Cu chromite.	Sauer and Adkins: <i>J. Am. Chem. Soc.</i> , 59, 1 (1937).



preferential reduction of the carboxyl group with retention of the ethylenic bond and the formation of an unsaturated alcohol, *e.g.*, ethyl oleate; T. 300°C.; yield, 50-60% octadecenol;  
 butyl oleate; T. 300°C.; yield, 65% octadecenol;  
 butyl oleate; T. 250°C.; yield, 86% octadecenol;  
 ethyl oleate; T. 250°C.; yield, 70% ethyl stearate.

Zn chromite.

Zn chromite.

Cu chromite.

Cu chromite.

Table 17. Catalytic Hydrogenation of Organic Acids.

Reaction	Catalyst	Observer
Hydrogenation of organic compounds:	Colloidal Rh (more active catalyst than noble metal catalysts such as Pt and Pd).	Zenghelis and Catherine Stathis: <i>Compt. rend.</i> , 206, 682-683 (1938).
(1) cinnamic acid to hydrocinnamic acid;		
(2) maleic acid and fumaric acid to succinic acid;		
(3) Benzonitrile to dibenzylamine, benzaldehyde (a small amount), and ammonia;		
(4) nitrobenzene to aniline;		
(5) acetone to isopropyl alcohol;		
(6) azobenzene to aniline (primary product) to cyclohexane and ammonia (secondary products) over $H_2$ ;		
(7) benzene to cyclohexane; hydrogenation carried out in water or absolute alcohol.		

Table 17 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of maleic acid to succinic acid.	NiCO <sub>3</sub> reduced on kieselguhr, Alundum or asbestos at 175–500° and under 80–165 mm. Hg pressure in the presence of H <sub>2</sub> ; these catalysts more active than those reduced at atmospheric pressure.	National Aniline and Chemical Co., Inc. (Coons): U.S.P. 2,120,958, June 14, 1938.
Hydrogenation of cinnamic acid and its esters; T. 100°; the ratio of hydrogenation velocity of cinnamic acid and oleic acid depends on whether Ni catalyst is used with or without a carrier.	5 7% Ni (without a carrier) shows considerably lower values than Ni on kieselguhr.	Kailan and Albert: <i>Monatsh.</i> , <b>72</b> , 169–178 (1938).
Catalytic hydrogenation of butyric acid to butanol or lauric acid to lauric alcohol under high partial pressure and at high temp.; the initial substances are used together with alcohols whose c.p. lies not more than 50° below the fatty acids used, and their amount is at least sufficient theoretically for the formation of a neutral ester.		Deutsche Hydrierwerke A.-G. (Rittmeister): G.P. 670,832, Kl 12o, Jan. 27, 1939.

Table 18. Catalytic Hydrogenation of Esters.

Reaction	Catalyst	Observer
Hydrogenation of aromatic esters, ethers and acids.	Ni <sub>2</sub> O <sub>3</sub> .	Ipatieff: <i>Ber.</i> , <b>41</b> , 1001 (1908).
Hydrogenation of esters to alcohols.	Ni, Cu—Cr oxide.	Adkins, Wojcik and Covert: <i>J. Am. Chem. Soc.</i> , <b>55</b> , 1669–1676 (1933).
Hydrogenation of esters of mono-basic or polybasic aliphatic carboxylic acids of more than one C atom; T. above 300°; pressure, at least 10 atm.; at 325° and under increased pressure, 1200 cc./hr. <i>n</i> -butyl acetate obtained.	Hydrogenation-promoting metals or metal oxides, such as reduced Cu, Sn, Cd or Pb and in certain cases Fe- or Ni-containing activators, such as Mn, Mg, Zn or Cr oxide; the chromates and chromites are particularly suitable for reduction processes, e.g., Cu—(NH <sub>4</sub> ) <sub>2</sub> CrO <sub>4</sub> is converted into copper chromite by heating; before using, it is reduced by treatment with H <sub>2</sub> .	Folkers and Adkins: <i>J. Am. Chem. Soc.</i> , <b>54</b> , 1145–1154 (1932).
Hydrogenation of Et mandelate; T. 175°; yield: 95% PhCH <sub>2</sub> CO <sub>2</sub> Et; T. 200°; yield: 70% PhCH <sub>2</sub> CH <sub>2</sub> OH and 13% PhEt; T. 200°; yield: 77% C <sub>6</sub> H <sub>11</sub> CH <sub>2</sub> CO <sub>2</sub> Et PhCH <sub>2</sub> CO <sub>2</sub> Et → C <sub>6</sub> H <sub>11</sub> CH <sub>2</sub> CO <sub>2</sub> Et T. 200°; yield: 94% T. 125°; yield: 77% Ph <sub>2</sub> C(OH)CH <sub>2</sub> O Ph <sub>2</sub> C(OH)CO <sub>2</sub> Et → Ph <sub>2</sub> C(OH)CH <sub>2</sub> O T. 200°; yield: 58% Ph <sub>2</sub> CHCH <sub>2</sub> OH and 38% Ph <sub>2</sub> CHMe Ph <sub>2</sub> CHCO <sub>2</sub> Et → Ph <sub>2</sub> CHCH <sub>2</sub> OH + Ph <sub>2</sub> CHMe	Ni. Cu—Cr oxide. Ni. Cu—Cr oxide.	
Hydrogenation of dialkyl esters of oxalic acid to glycol; T. 201–275°; pressure, 200–1000 atm.; e.g., C <sub>2</sub> O <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> to ethylene glycol; T. 240–260°.	Cu chromite.	Dupont (Lazier): U.S.P. 2,000,880, Nov. 17, 1936.
Hydrogenation of esters of fatty acids to higher aliphatic alcohols; high temp. and pressure.	Commercial CuCO <sub>3</sub> .	Böhme Fettchemie Gesellschaft m.b.H. (Normann): G.P. 642,518, Kl 12o, March 10, 1937.

Table 19. Catalytic Hydrogenation of Benzene.

Reaction	Catalyst	Observer
Hydrogenation of benzene to cyclohexane.	Ni.	Sabatier and Senderens: <i>Ann. chim. phys.</i> (8), <b>4</b> , 334 (1905).
Hydrogenation of benzene to cyclohexane.	Pt.	Willstätter and Hatt: <i>Ber.</i> , <b>45</b> , 1471-1481 (1912).
Hydrogenation of benzene to cyclohexane.	Pd.	G.P. 272,340, Kl 120, March 28, 1914.
Hydrogenation of benzene to cyclohexane.	Pd.	Hinrichsen and Kempf: <i>Ber.</i> , <b>48</b> , 2106 (1915).
Hydrogenation of benzene to cyclohexane.	Ni.	Tetralin G.m.b.H.: G.P. 305,104 (1916).
Hydrogenation of benzene to hexahydrobenzene.	NiO + Al <sub>2</sub> O <sub>3</sub> .	Pfaff and Brunck: <i>Ber.</i> , <b>56</b> , 2463 (1923).
Hydrogenation of benzene to hexahydrobenzene.	NiO + Al <sub>2</sub> O <sub>3</sub> .	Zelinsky and Komarewski: <i>Ber.</i> , <b>57</b> , 667 (1924).
Hydrogenation of benzene to cyclohexane.	Cu (obtained by slow reduction of CuO at 150°).	Pease and Purdum: <i>J. Am. Chem. Soc.</i> , <b>47</b> , 1435-1442 (1925).
Hydrogenation of benzene to tetrahydrobenzene.	Ni—kieselguhr.	Schoorel, Tulleners and Waterman: <i>J. Inst. Petroleum Tech.</i> , <b>18</b> , 179 (1932).
Hydrogenation of benzene to tetrahydrobenzene.	Ni(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O precipitated with Na <sub>2</sub> CO <sub>3</sub> at 70-80°; reduced with H <sub>2</sub> at 450°.	Adkins and Cramer: <i>J. Am. Chem. Soc.</i> , <b>52</b> , 4349 (1930).
Hydrogenation of benzene to cyclohexane.	Ni > Co > Cu > Ru > Rh > Ir > Os > Pd > Pt; activity decreases as the shortest atomic distance moves away from the extremities; Ni, smallest; Pt, largest.	Westling: <i>Chem. News</i> , <b>143</b> , 35-39 (1931).
Hydrogenation of benzene to cyclohexane; T. 180-185°; at 250-300°, yield of saturated hydrocarbons, 75-90%; at 300°, chiefly CH <sub>4</sub> .	Ni and Pt; Pt gives the same result as Ni but at a smaller streaming velocity.	Bancroft: <i>J. Phys. Chem.</i> , <b>35</b> , 2219-2225 (1931).
Hydrogenation of benzene to cyclohexane.	Cu—Cr or Zn—Cr obtained by surface oxidation of their alloys with HNO <sub>3</sub> , or anodic surface oxidation.	Maxted: E.P. 378,943, Sept. 15, 1932.
Hydrogenation of benzene to cyclohexane; temp., up to 440°; dibenzyl not hydrogenated up to 300°; stilbene converted into dibenzyl at a temp. greater than 270°.	NaH.	Hugel and Friess: <i>Ann. combustibles liquides</i> , <b>6</b> , 1109-1147 (1932).
Hydrogenation of benzene to cyclohexane under high pressure.	NiO.	Tanaka, Kobayashi, Endo and Fujita: <i>J. Soc. Chem. Ind. Japan</i> , <b>37</b> , 538B-539B (1934).
Hydrogenation of benzene to cyclohexane (at ordinary temp., insignificant) between gaseous H <sub>2</sub> , containing the heavy H <sub>2</sub> isotope in marked conc. (1.14-20.9%) and benzene, a very active exchange of H <sub>2</sub> atoms takes place in which the heavy H <sub>2</sub> isotope in the gaseous phase is replaced by the light H <sub>2</sub> isotope from benzene.	Pt or Ni.	Horiuti, Ogden and Polanyi: <i>Trans. Far. Soc.</i> , <b>30</b> , 663-665 (1934).
Hydrogenation of benzene to cyclohexane.	Asbestos containing about 30% Pt (obtained by reduction with HCHO).	
Hydrogenation of benzene to cyclohexane.	Colloidal Pt (with gum arabic as protective colloid).	
Hydrogenation of benzene to cyclohexane; T. 460°; pressure, 50-250 atm. H <sub>2</sub> .	MoS <sub>3</sub> .	

Table 19 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of aromatic hydrocarbons (benzene, toluene, o-xylene, mesitylene and duroil); T. room-250°; pressure up to 250 atm. at 75-230°; the hydrogenation reaction proceeds with a constant velocity and is therefore of the zero order with respect to the hydrocarbons if conversion does not exceed 60-70%; if higher conversion, the velocity decreases because catalyst surface is covered with naphthenic products formed during the reactions; the influence of H <sub>2</sub> pressure upon reaction velocity (in case of toluene) depends on the temp.; below 110° the velocity is independent of the H <sub>2</sub> conc.; with increasing temp. the pressure influences the velocity in a positive sense; at 190-200° the velocity of hydrogenation of toluene is proportional to the H <sub>2</sub> pressure within 20-140 atm.; the temp. influence in case of benzene and toluene indicates similar influence for both aromatics; the increase of velocity with increasing temp. (75-100°) becomes always smaller; in the temp. interval 190-210°, the hydrogenation reaction proceeds with maximum velocity independent of temp.; in this field the temp. coefficient is about 1.	Ni + Al <sub>2</sub> O <sub>3</sub> .	Losowoi and Djakowa: <i>Zhur. Obshchei Khim.</i> , 7 (69), 2964-2977 (1937).
Hydrogenation of n-hexanol, benzene; naphthalene; a mixture of n-hexanol and H <sub>2</sub> with 3% CS <sub>2</sub> or S to hexane; 8-12 hrs. duration; yield, 45.7% 74.6% 89.2% 93.5% 97.6% 95.2%	Fe <sub>2</sub> O <sub>3</sub> /MgO Fe <sub>2</sub> O <sub>3</sub> MoO <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> /2Al <sub>2</sub> O <sub>3</sub> Bauxite	Fuchs and Brendlein: <i>Angew. Chem.</i> , 52, 49-58, 14/I (1939).
Hydrogenation of benzene; T. 225°; ordinary pressure.	Cu containing 0.1% Ni; Cu + 3.5% Cr <sub>2</sub> O <sub>3</sub> has a much higher activity than pure Cu; catalytic properties of Cu disappear at 350-400°.	Ipatieff, Corson and Kurbatov: <i>J. Phys. Chem.</i> , 43, 589-604 (1939).
Hydrogenation of benzene.	Pure Cu prepared from the hydroxide or basic carbonate with at least 0.2% O <sub>2</sub> or water hydrogenates well under pressure, but very slowly at atmospheric pressure; wholly pure copper is inactive; the Cr oxide increases catalytic activity of Cu by surface increase; highest activity is claimed for the composition: 95% Cu + 5% Cr <sub>2</sub> O <sub>3</sub> .	Friedwald: <i>Rev. petrolière</i> , 1939, 765-66 (refer to works of Ipatieff and Sabatier).
Hydrogenation of aromatic hydrocarbons, e.g., benzene, into cyclohexane at room temp. on account of H <sub>2</sub> liberated in the reaction: $\text{Ca}(\text{NH}_2)_2 \rightarrow \text{Ca}(\text{NH}_2)_2 + \text{H}_2 + 4\text{NH}_3$		Kasanski and Gluschnew: <i>Zhur. Obshchei Khim.</i> , 8 (70), 642-50 (1938).

Table 20. Catalytic Hydrogenation of Benzene.

Reaction	Catalyst	Observer
Catalytic conversion of Baku and Grozny (white spirit) benzines SB-96, in which cracking, formation of polymers and isomers, hydrogenation and dehydrogenation and also destructive alkylation take place in the benzines with less than 10% boiling parts up to 100° are in part subjected to catalysis 3 times after which more than 44% boiling parts up to 100° are obtained, rich in isoparaffins with greatly increased octane number (96) as against 65 of the initial material.	AlCl <sub>3</sub> .	Feigin, Kolomatzki and Tarasowa: <i>Nefityanoe Khos.</i> , 12 (6), 38-42 (1938).
Hydrogenation of benzines; influence of the crude catalyst and working method discussed.		Pier: <i>Angew. Chem.</i> , 51, 603-608, Sept. 10, 1938.
Hydrogenation of cracking benzines (dehydrogenation of cyclohexane to benzene); (aromatization of benzene).	A mixture of Cr oxides and Cr sulfides obtained by reduction of Cr sulfate or Cr alum with H <sub>2</sub> .	Moldawski and Kamuscher: <i>Russ. P.</i> 53,573, July 31, 1938.

Table 20 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of benzene (in gaseous phase); the catalysts investigated behave similarly in hydrogenation of benzene and in dehydrogenation of cyclohexane.	(1) Ni and Co have a promotion effect of the same order caused by traces of the oxide; (2) Ni with admixture of Fe, Cu, or Cd has no catalytic activity; the same holds for partially reduced mixtures $\text{NiO-Fe}_2\text{O}_3$ and $\text{NiO-CdO}$ ; Ni-Co mixtures have promoter action of the order of pure metals; (3) Ni with traces of K salt does not increase activity; traces of Li or MgO increase it between 100-200°; (4) small amounts of $\text{CaCO}_3$ or $\text{BaCO}_3$ decrease promoter action of Ni; (5) binary catalysts; mixtures $\text{Ni-Al}_2\text{O}_3$ , $\text{Ni-Cr}_2\text{O}_3$ , $\text{Ni-CeO}_2$ , $\text{Ni-BeO}$ and $\text{Ni-Zn}$ are much more active than pure Ni; (6) addition of small amounts of $\text{Al}_2\text{O}_3$ , $\text{Cr}_2\text{O}_3$ , or $\text{ZnO}$ to Co increase catalytic activity.	Juliard and Herbo: <i>Bull. soc. chim. Belg.</i> , <b>47</b> , 717-69 (1938).
Pressure hydrogenation of benzines; petroleum fractions, c.p. about 180-370°, are subjected at 480° and 50 atm. to strong cracking; a residue is obtained which at 50° has a density above 1; this residue is subjected to hydrogenation under more than 300 atm., especially at 475° and 600 atm.; benzines with an octane number 65-70 and gas oils with a cetene number 30 are obtained; these may be improved by refined pressure hydrogenation over catalysts to gas oils having a cetene number of about 50.	Mixture of sulfides of W and Fe.	N. V. International Hydrogenation Maatschappij: F.P. 839,358, April 3, 1939.
	Sulfides of W and Ni.	
Hydrogenation of olefin polymers; polymer benzines are hydrogenated at 150-500°, especially 150-300° over catalysts to saturated hydrocarbons.	Fe, Ni, Co activated with $\text{ThO}_2$ , $\text{Ce}_2\text{O}_3$ , $\text{ZrO}_2$ , or $\text{TiO}_2$ ; a catalyst of Ni activated with 10% $\text{ThO}_2$ and precipitated on pumice is said to be especially active.	Shell Development (Taylor, M. D.): Can. P. 379,927, March 1939.

Table 21. Catalytic Hydrogenation of Benzene Derivatives.

Reaction	Catalyst	Observer
Hydrogenation of hexahydrophenol to tetrahydrobenzene under high pressure.	Alumina.	Ipatieff: <i>Ber.</i> , <b>42</b> , 2089 (1909). Ipatieff: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>37</b> , 1296 (1905).
Hydrogenation of hydrobenzene to hexahydrobenzene; T. 330° pressure, 125 atm.	3 g. $\text{CuO}$ (in an iron apparatus).	Ipatieff: <i>Ber.</i> , <b>43</b> , 3387 (1910).
Hydrogenation of parachloronitrobenzene to chloraniline; T. 238°; no nitrobenzene formed; N—O bond more readily broken and hydrogenated than the C—Cl bond.	Ni.	Balandin and Titowa: <i>Izvest. Akad. Nauk U.S.S.R.</i> , <b>2</b> , 229-231 (1934).
Hydrogenation of crude benzene derivatives: styrene, indene, and naphthalene; T. 125-145°; to prevent conversion into resins, process is carried out in either vapor or liquid phase or in both, e.g., vapors are led optionally at 115°, 130°, 140° and 150° with addition of fresh $\text{H}_2$ over the catalyst under a pressure of $1\frac{1}{4}$ atm.	Ni.	Gwynn: U.S.P. 2,106,735, Feb. 1, 1938. refer also to U.S.P. 2,073,578, March 9, 1937.

Table 22. Catalytic Hydrogenation of Phenols.

Reaction	Catalyst	Observer
Hydrogenation of phenol.	Ni <sub>2</sub> O <sub>3</sub> .	Ipatieff: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>38</b> , 45 (1906). Ipatieff: <i>Ber.</i> , <b>40</b> , 1827 (1907).
Hydrogenation of phenol to cyclohexanol in the presence of H <sub>2</sub> .	Cu	Goldsmith: B.P. 17,573 (1906). Tetralin G.m.b.H. (Schroeter): G.P. 299,013 (1916).
Hydrogenation of phenols with unsaturated side chains under pressure; saturation of the double bond takes place, followed by hydrogenation of aromatic nucleus; addition of H <sub>2</sub> to the double bond occurs at 95°.	Reduced Ni.	Ipatieff: <i>Ber.</i> , <b>46</b> , 3589-93 (1913).
Hydrogenation of phenol to cyclohexanol in the presence of H <sub>2</sub> .	Ni.	Brochet: E.P. 16,936 (1913). E.P. 22,523 (1913).
Hydrogenation of phenol to cyclohexanol in the presence of H <sub>2</sub> .	Ni + Cu.	Tetralin G.m.b.H. (Schroeter): G.P. 299,012 (1916). G.P. 299,013 (1916).
Hydrogenation of polyatomic phenols (pyrocatechin).	Ni <sub>2</sub> O <sub>3</sub> .	Ipatieff and Lugovoy: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>46</b> , 470 (1914).
Hydrogenation of polyatomic phenols to quinones.	Magnetic catalysts.	Walter: G.P. 295,507, Kl 12g Gr 2, April 20, 1913.
Hydrogenation of phenol in the presence of H <sub>2</sub> .	Na <sub>2</sub> CO <sub>3</sub> (solid catalyst).	Armstrong and Hilditch: <i>Proc. Roy. Soc. London (A)</i> , <b>102</b> , 21-7, 28-32 (1921).
Hydrogenation of phenol.		Schrauth: <i>Z. angew. Chem.</i> , <b>35</b> , 617 (1922). Schrauth: <i>Ber.</i> , <b>56</b> , 261 (1923).
Hydrogenation of phenols (mechanism).		Vavon and Berton: <i>Bull. soc. chim.</i> , <b>37</b> , 296-305 (1925).
Hydrogenation of amino-phenols to cyclic amino-alcohols.	Pt oxide.	Heckel and Adams: <i>J. Am. Chem. Soc.</i> , <b>47</b> , 1712-1718 (1925).
Hydrogenation of halogen phenols to phenol.	Ni, Co, Cu, Mn, Ni—Cu, Ni—Mn.	Rheinische Kampfer Fabrik (Schöllkopf): G.P. 432,802, Kl 12g, Aug. 11, 1926.
Hydrogenation of phenols (mechanism).		Grignard and Mignon: <i>Compt. rend.</i> , <b>185</b> , 1552-1556 (1927).
Hydrogenation of phenols under high pressure.	MoO <sub>3</sub> , MoS <sub>3</sub> , (NH <sub>4</sub> ) <sub>2</sub> S <sub>4</sub> , NiS, CoS.	Tropsch: <i>Proc. Intern. Conf. Bituminous Coal, 3rd Conf.</i> , <b>2</b> , 35-48 (1931).
Hydrogenation of <i>o</i> -cresol in presence of benzoic acid; T. 195°; time, 3 hrs.; yield 82% pure <i>o</i> -tolyl benzoate; H <sub>2</sub> O removed as fast as formed, using CaOCl <sub>2</sub> .	Surface catalysts: (ZnFe)O · Fe <sub>2</sub> O <sub>3</sub> or ZnO · Fe <sub>2</sub> O <sub>3</sub> (Franklinite).	Rheinische Kampfer Fabrik (Skraup): G.P. 565,969, March 15, 1931.
Hydrogenation of phenols.	CoS; Co <sub>2</sub> O <sub>4</sub> obtained from CoS by reduction with very active catalyst.	Gaglietti and Roberti: <i>Gazz. chim. ital.</i> , <b>62</b> , 19-29 (1932).
Hydrogenation of crude phenol mixtures to polyatomic phenols.	Mn or Co acetate.	I. G. Farbenindustrie A.-G. (Weber, Grienbach and Münch): G.P. 555,936, Kl 12g, Aug. 3, 1932.
Hydrogenation of phenols; preheated before reaction up to 375°; temp. increased to 400-500°; reaction temp. not exceeding 450°; pressure, up to 500 atm.	Mo.	Imperial Chemical Industries, Ltd. (Madel and Huntley): E.P. 378,501, Sept. 8, 1932.

Table 22 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of crude phenol mixtures (tars): T. 485°; time, 5½ hrs.; pressure, 90 atm. H <sub>2</sub> ; yield, 51% phenols (including pure phenol and cresols, about equal in amount), 34% neutral oil (including benzene and toluene, about equal in amount), about 15% H <sub>2</sub> O.	None.	Hofmann and Lang: G.P. 553,410, Kl 12o, June 29, 1932.
Hydrogenation of cresols with simultaneous reduction of the OH-group, followed by hydrogenation of aromatic nucleus; splitting of the CH <sub>3</sub> radical also occurs; low temp. favorable; independent of the nature of the catalyst.	Sulfides of Mo, W, Co, Ni, Fe. Oxides of Mo, V, U, Zn (WO <sub>3</sub> inactive). Hydroxides of Co, Fe, Al, Cr.	Tropsch: <i>Fuel</i> , <b>11</b> , 61-66 (1932).
Hydrogenation of crude phenol mixtures: T. 250-400°; pressure, greater than 20 atm. and less than 100-200 atm.; only a small part of the phenols converted into hydrocarbons; S- and N- containing impurities split off.	Metals of the 6th or 8th group.	I. G. Farbenindustrie A.-G.: F P. 738,100, Dec. 20, 1932.
Hydrogenation of phenols and cresols, especially tar acids, under pressure, to hydrocarbons used as motor fuel.	Mo.	Matthews and Newell: E.P. 371,851, May 26, 1932.
Hydrogenation of phenol in presence of H <sub>2</sub> : T. 0°; initial pressure, 69 atm.; at 150-250°, cyclohexanol formed; at 360°, intermediate products, such as cyclohexanone, cyclohexane, cyclohexene and benzene, obtained by heating cyclohexanol in N <sub>2</sub> at 310° in presence of a dehydrating catalyst, Al <sub>2</sub> O <sub>3</sub> .	Reduced Ni.	Ando: <i>J. Soc. Chem. Ind. Japan</i> , <b>35</b> , 455-458 (1932).
Hydrogenation of cresols and dihydroxyphenols.		Cawley: <i>Fuel</i> , <b>12</b> , 29-35 (1933).
Hydrogenation of technical phenols in vapor phase.	Ni with 25% Na <sub>2</sub> CO <sub>3</sub> added.	Belozerkowski: <i>Plasticheskie Massy</i> , <b>3</b> , 12-16 (1935). Armstrong: (Refer to C. 1922 III 1322).
Hydrogenation of phenols; T. 175-180°; yield, 75% cyclohexanol, 15% cyclohexanone, 6% phenol, 4% benzene and hexane; T. 280°; yield, 70% methylcyclohexanone, 20% methylcyclohexane, 7% cresol, 3% toluene and methylhexane.	Ni formate on chamotte (stable; no fatigue during 15 days' test run); chamotte impregnated with 10-15% Ni(NO <sub>3</sub> ) <sub>2</sub> reduced in the presence of H <sub>2</sub> at 200-250°; 150 g. 6% Ni containing chamotte; Cu cylinders serve as contact chamber.	Snelling: U.S.P. 1,122,811. Sabatier.
Hydrogenation of phenols under pressure; T. 455°; a small amount of benzene formed; cyclohexanol, intermediate product, converted into cyclohexane and methylcyclopentane, passing through cyclohexane.	Mo oxide.	Ando: <i>J. Soc. Chem. Ind. Japan</i> , <b>36</b> , 33B-38B (1933).
Hydrogenation of phenols under high pressure and phenolic acids (oils) from low-boiling tars; T. 350°; initial pressure, 47-73 atm. H <sub>2</sub> .	MoO <sub>3</sub> .	Ando: <i>Ibid.</i> , <b>36</b> , 243B-244B (1933).
Hydrogenation of phenols to hydrocarbons; T. 360-430°; pressure, 5-20 atm.	Elements of the 3rd, 4th and 6th groups; activated Al <sub>2</sub> O <sub>3</sub> together with oxides of Mo, W and Cr.	Société des Carburants Synthétiques: F.P. 750,697, Aug. 6, 1933.



Table 22 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of alkali salts of phenols to hydroaromatic alcohols in liquid phase.	Ni.	Shering-Kahlbaum (Schwenk and Jordan): G.P. 571,972, Kl 120, March 9, 1933.
Hydrogenation of O <sub>2</sub> -containing cpds., such as phenols, to toluene and methylcyclohexane; T. 400°; initial pressure, 15-40 atm.	MoS <sub>2</sub> ; refining crude kerosene with loam: MoS <sub>2</sub> =90:10 at 40-70 atm. pressure.	Moldawski and Liwischitz: <i>Khim. Tverdogo Topliwa</i> , <b>5</b> , 91-96 (1934).
Hydrogenation of phenol and tricresol; T. 480° pressure, 100 atm.; a large amount of low-boiling hydrocarbons formed; if more S is used, hydroaromatics and saturated hydrocarbons are obtained; if less S tricresol is more readily hydrogenated than phenol.	MoO <sub>3</sub> (in the presence of flowers of sulfur (0-16%), action more energetic; S converted into H <sub>2</sub> S during the reaction).	Bognar: <i>Magyar Chem. Folyoirat</i> , <b>40</b> , 105-112 (1934).
Hydrogenation of phenol.		Bag. Egupow and Wolokitin: Russ. P. 39,767, Nov. 30, 1934; add to Russ. P. 23,523 C (1932).
Destructive hydrogenation of phenols obtained from a coal-tar fraction (b.p. 325°) containing 56.86% phenol and 38.77% neutral oil; T. 400-440°; pressure, 40-150 atm. H <sub>2</sub> .	MoS <sub>2</sub> .	Rapoport, Mintshenkov and Konow: <i>Khim. Tverdogo Topliwa</i> , <b>6</b> , 146-161 (1935).
Hydrogenation of resorcin at room temp.; reduction proceeds irregularly; hexahydroresorcin, cyclohexanol and cyclohexane formed, but these compounds originate one after another in parallel reactions.	PtO <sub>2</sub> (in the case of an active catalyst, the mutual distances of its active centers are small; hence an adsorbed molecule on the catalyst saturates its double bonds; also, due to proximity to unadsorbed atomic groups, such as OH, the catalyst is brought into reaction with H <sub>2</sub> ; in the case where the mutual distances of its active centers are large, only the adsorbed particles of the molecule are saturated).	Packendorff: <i>Ber.</i> , <b>68</b> , 125-154 (1935).
Hydrogenation of octyl phenol (100 parts) in decahydronaphthalene to 4-octylcyclohexanol; T. 175°; pressure, 40 atm. H <sub>2</sub> .	Ni (5 parts).	Henkel and Co.: E.P. 461,957, March 25, 1937.
Hydrogenation of mononuclear and polynuclear phenols to the corresponding cyclic secondary alcohols in liquid or vapor phase; <i>p</i> -phenylphenol to phenylcyclohexanol (1); <i>p</i> -phenylphenol to cyclohexylcyclohexanol (2).	Cu chromate (1). Ni chromate (2) (catalysts prepared by heating a multiple chromate of a hydrogenating metal and a N base to its spontaneous decomposition temp.; decomposition T. 200-400°; reduction T. 500°).	Dupont (Lazier): U.S.P. 2,087,691, July 20, 1937.
Hydrogenation of phenols in the hydroxyl-containing nucleus; process passes through the tautomeric ketone.	Cu—Cr oxide.	Musser and Adkins: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 164-169 (1938).
Hydrogenation of dihydroxyphenols, such as resorcin; T. 180°; a small amount of hexahydroresorcin, in addition to cyclohexane and phenol, obtained.	Ni.	Sabatier and Maible: <i>Ann. chim.</i> (8), <b>16</b> , 92 ( ).
Hydrogenation of dihydroxyphenols, such as resorcin, to oxyderivatives of diphenylene oxide.	WO <sub>3</sub> .	Tsuzuki: <i>Bull. Chem. Soc. Japan</i> , <b>2</b> , 79-83 (1933). (Refer to C. 1934 I 53).
Catalytic hydrogenation of phenols under high pressure.		Ando: <i>J. Fuel Soc. Japan</i> (2), <b>17</b> , 87-96 (1938).

Table 23. Catalytic Hydrogenation of Toluene and Xylene.

Reaction	Catalyst	Observer
Hydrogenation of toluene.	Ni on kieselguhr.	Adkins and Covert: <i>J. Phys. Chem.</i> , <b>35</b> , 1684 (1931).
Hydrogenation of toluene; T. up to 460°; pressure, 50 to 250 atm. H <sub>2</sub> .	MoS <sub>2</sub> ; magnitude of the apparent activation energy is constant at 400–460° and is equal to 23–100 kg./cal.	Altmann and Nemzow: <i>Acta Physicochim. U.R.S.S.</i> , <b>1</b> , 429–448 (1934).
Hydrogenation of toluene to methylcyclohexane in the presence of ethyl alcohol; T. 170–210°; toluene is reduced to aldehyde due to the dehydrogenation of ethyl alcohol; ratio of alcohol to toluene, 9 : 1; T. 190°; yield, 26%.	Ni on Al <sub>2</sub> O <sub>3</sub> .	Schujkin and Feder: <i>Zhur. Priklad. Khim.</i> , <b>7</b> , 1192 (1934).
Hydrogenation of xylene; T. 180–200°; pressure, 15–30 atm. H <sub>2</sub> .	NiO, CuO, MnO <sub>2</sub> dissolved in hexahydroxylene precipitated on kieselguhr.	A.-G. für Anilin Fabrikation: G.P. 383,540 (1923).
Destructive hydrogenation of xylene and solvent naphtha (equimolecular amounts) in a stream of H <sub>2</sub> ; T. 330–400°; with xylene predominating, 38.9% benzene-toluene fraction and 38.4% toluene-xylene fraction obtained; in addition, considerable decomposition into CH <sub>4</sub> and essential C precipitation; with solvent naphtha predominating (limit, b.p. 150–230°) 17.8% of a fraction at 80–150° consisting of 91.5% aromatics obtained.	Among catalysts, Ni, Cu, Cu on Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , or asbestos, only Ni active and namely 50% Ni + Al <sub>2</sub> O <sub>3</sub> dried at 125°; reduced in series at 270°, 300°, 330° and 350° until the formation of H <sub>2</sub> O is no longer observed; NiSiO <sub>2</sub> less intensive and smaller losses.	Schujkin: <i>Zhur. Priklad. Khim.</i> , <b>10</b> , 652–659 (1937). Zelinsky and Komarevsky: <i>Ber.</i> , <b>57</b> , 667 (1924).

Table 24. Catalytic Hydrogenation of Various Acids.

Reaction	Catalyst	Observer
Hydrogenation of phthalic acid to hexahydrophthalic acid.	Ni <sub>2</sub> O <sub>3</sub> .	A. von Bayer: <i>Ann. chim.</i> , <b>259</b> , 214 (1890).
Hydrogenation of monobromhexahydrophthalic acid to hexahydrophthalic acid.	Na—Hg.	
Hydrogenation of benzoic or phthalic acid to benzaldehyde in the presence of H <sub>2</sub> (industrial process).	Fe + Ce—(Co).	I. G. Farbenindustrie A.-G.: E.P. 267,925 (1927). F.P. 627,920 (1927).
Hydrogenation of cinnamic acid.	Pd on blood charcoal 9 times more active than when precipitated on kieselguhr.	Rosemund and Langer: <i>Ber.</i> , <b>56</b> , 226 (1923).
Hydrogenation of cinnamic and oleic acids, as well as eugenol, coumarin, etc.; T. 115–120°; using Tetralin as a H <sub>2</sub> donor; hydrocinnamic acid, stearic acid, hydroeugenol and hydrocoumarin obtained.	Pd black.	Akabori and Suzuki: <i>Proc. Imp. Acad. (Tokyo)</i> , <b>5</b> , 255–256 (1930).
Hydrogenation of maleic and fumaric acids, also sodium cinamate.	Blood charcoal > bone charcoal > sugar charcoal > kieselguhr.	Sabalitschka and Moses: <i>Ber.</i> , <b>60</b> , 786 (1927).
Hydrogenation of maleic acid in liquid phase; T. 15–20°.	Rh on ring shaped ceramic carrier; (weak for hydrogenation, but active for dehydrogenation of alcohol); perrhenates and rhenium alloys may prove more effective.	Platonow, Anissimow and Krascheninnikowa: <i>Ber.</i> , <b>68</b> , 761–765 (1935).
(1) Hydrogenation of the sodium salts of aromatic acids to polymethylene acids at high pressure.	(1) NiO.	Ipatieff: <i>Ber.</i> , <b>41</b> , 1003 (1908); <b>42</b> , 2091 (1909).
(2) Hydrogenation of the aromatic nucleus does not take place.	(2) CuO or reduced Cu.	
Hydrogenation of unsaturated $\alpha$ -keto acids, aldehydes and alcohols.	Fermenting yeast.	Fischer and Wiedemann: <i>Ann.</i> , <b>513</b> , 260–280 (1934).

Table 24 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of sorbic acid to $\alpha$ -hexane, $\Delta$ , $\alpha$ -hexene acid and small amounts of $\Delta$ , $\beta$ - and $\Delta$ , $\gamma$ -hexene acid.	Spongy Ni or Pt electrodeposited on polished Ni and Pt cathodes; Adams Pt catalyst in alcohol gives the same reduction products in about the same ratio.	Isaacs and Wilson: <i>J. Chem. Soc.</i> , 1936, 574-576.
Hydrogenation of crotonic acid purified by repeated sublimation below 100° and treatment with excess Pt black; T. 19-110°; (the graphic presentation of the course of reaction, showing amount of H <sub>2</sub> adsorbed plotted against time, gives at temp. below the inversion point, a straight line indicating a sharp break characteristic of a reaction of zero order; at temp. above the inversion point the curves correspond to a reaction of the first order; therefore an increase in temp. introduces a factor which causes a change in the reaction order).	Pt.	Maxted and Moon: <i>J. Chem. Soc.</i> , 1936, 635-637. ZurStrassen: <i>Z. physik. Chem.</i> (A), 169, 81-90 (1934). (Refer to C. 1934 II 2039). Schwab and Brennecke: <i>Ibid.</i> , (B), 24, 393 (1934). (Refer to C. 1934 I 3306).

Table 25. Catalytic Hydrogenation of Oxygen-containing Organic Compounds.

Reaction	Catalyst	Observer
Hydrogenation of diphenyl oxide to dicyclohexyl.	Ni + Al <sub>2</sub> O <sub>3</sub> .	Ipatieff and Orloff: <i>Compt. rend.</i> , 181, 793 (1925).
Hydrogenation of diphenyl oxide to phenol; T. 450-460°.	Active charcoal or silica gel.	Gesellschaft für Teerverwertung: G.P. 545,583 (1931).
Hydrogenation of mesityl oxide under pressure; at, or less than 140°; 2-methylpentanone obtained; at 170-210°, 2-methylpentanol is formed.	Ni.	Deutsche Gold und Silber Scheideanstalt: B.P. 362,457, Dec. 23, 1930.
Hydrogenation of O <sub>2</sub> -containing organic cpds.	Prepared from oxalates by thermal decomposition in an oxidizing atmosphere; mixtures of oxalates when decomposed partially form metallic oxides, metallic carbonates and metals.	Canadian Industries, Ltd.: Can. P. 320,784, March 22, 1932.
Hydrogenation of O <sub>2</sub> -containing organic cpds., for example, phenols, to toluene and methyl cyclohexane in a rotating autoclave; purification with H <sub>2</sub> SO <sub>4</sub> not necessary; T. 400°; initial pressure, 15-40 atm.	MoS <sub>2</sub> .	Moldawski and Liwschitz: <i>Khim. Tverdogo Topliva</i> , 5, 91-96 (1934).
Hydrogenation of oxides of C cpds. at high temp. and pressure.	V, Nb, Ta, or their alloys, or mixtures containing them with the exception of contact masses; quoted in G.P.*	I. G. Farbenindustrie A.-G. (Mittasch and Pier): G.P. 637,446, Kl 12o, Oct. 28, 1936. G.P. 600,677 *G.P. 636,682 (1936).
Hydrogenation of oxides of hydrocarbons, e.g., a mixture of 28-29% CO, 56-60% H <sub>2</sub> , and the remainder CO <sub>2</sub> and N <sub>2</sub> ; T. 185-190°; after 24 hr. temp. decreased to 180-185°; time, 1 hr.; under H <sub>2</sub> pressure; high molecular paraffins obtained; composed in part of high-boiling products and CH <sub>4</sub> ; the non-volatile products originating in the catalytic reaction are removed at short intervals when precipitated on the catalyst and before they influence it markedly.	Co, Th, kieselguhr.	I. G. Farbenindustrie A.-G. (Mittasch and Pier): (Refer to C. 1934 II 2284).
		Ruhrchemie A.-G.: F.P. 812,883, May 19, 1937. Ital. P. 346,389, Nov. 16, 1936. Indian P. 23,662, Sept. 17, 1937.

Table 25 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of (1) oxymethylene cyclohexanone;	(1) Na. amalgam in acetic acid solution.	Rupe and Klemm: <i>Helv. Chim. Acta</i> , <b>21</b> , 1538-1541, Dec. 1, 1938.
$\begin{array}{c} \text{H}_2\text{C} \cdot \text{CH}_2 \cdot \text{CO} \\   \\ \text{H}_2\text{C} \cdot \text{CH}_2 \cdot \text{C} : \text{CH} \cdot \text{OH} \end{array} \rightarrow (\text{CH}_2)_2 \begin{array}{c} \text{CH} \cdot \text{OH} \\   \\ \text{CH} \cdot \text{CH}_2\text{OH} \end{array} \rightarrow (\text{CH}_2)_2 \begin{array}{c} \text{CH} \cdot \text{O} \\   \\ \text{CH} \cdot \text{CH}_2 \end{array}$		
(2) obtained in a small yield; (3) isoamyl formate obtained from cyclohexanone; yield, 83%; (4) oxymethylcyclohexanol, $\text{C}_7\text{H}_{14}\text{O}_2$ , obtained from oxymethylenecyclohexanone and $\text{H}_2$ ; yield, 88%.	(2) heating with dilute $\text{H}_2\text{SO}_4$ ; (3) Na in ether (c.p. 85-87); (4) Ni in dilute alcohol.	

Table 26. Catalytic Hydrogenation of Aromatic Amines.

Reaction	Catalyst	Observer
Hydrogenation of aromatic amines.	NiO.	Ipatieff: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>40</b> , 491 (1908).
Hydrogenation of cyclic aminophenols to cyclic amino-alcohols.	Pt oxide.	Heckel and Adams: <i>J. Am. Chem. Soc.</i> , <b>47</b> , 1712-1718 (1925).
Hydrogenation of aromatic amines.	Pt oxide, Pt black.	Hiers and Adams: <i>Ber.</i> , <b>59</b> , 140-162 (1926).
Hydrogenation of diphenylamines and triphenylamines.	Pt oxide, Pt black.	Hiers and Adams: <i>J. Am. Chem. Soc.</i> , <b>49</b> , 1099-1103 (1927).
Hydrogenation of monoamines of the benzene series.	An alkali metal, an alkaline-earth metal, an alkali salt of a weak acid, such as $\text{Na}_2\text{CO}_3$ , or an alkaline-earth oxide or hydroxide inhibit the formation of by-products.	General Aniline Works (Lommel and Goost): U.S.P. 1,927,130, Sept. 19, 1933.
Hydrogenation of primary amines; T. 175-250°; high pressure; (1) aniline; T. 175°; pressure, 150-240 atm.; time, 5-8 hrs.; yield, 80% cyclohexylamine (25% aniline remains unchanged). (2) $\beta$ -naphthylamine-benzidine in the presence of methylcyclohexane as a solvent.	Soluble Ni impregnated on kieselguhr and treated with a basic carbonate; $\text{NiCO}_3$ precipitated is reduced; Ni precipitated on silica.	Goodyear Tire and Rubber Co.: F.P. 750,903, Aug. 22, 1933.
Hydrogenation of aryl-naphthylamines in liquid phase: 150 g. freshly distilled phenyl- $\alpha$ -naphthylamine to phenyltetrahydro- $\alpha$ -naphthylamine; T. 120°; initial pressure, 26 atm. $\text{H}_2$ .	Raney's Ni.	Wingfoot Co. (Winans): U.S.P. 2,095,897, Oct. 12, 1937.
Hydrogenation of mixtures of binary HCl-containing pyridine bases in absolute alcohol; predominant hydrogenation of pyridine and $\alpha$ -picoline is ascertained; $\alpha$ -, $\beta$ -, and $\gamma$ -picoline, $\alpha$ -, $\alpha'$ -lutidine and quinoline react in binary mixtures only afterwards in the mixture of 3 picolines; the components are hydrogenated simultaneously.	Pt black.	Ushakow, Iwanowa, Kaschelewa: <i>Zhur. Obshchei Khim.</i> , <b>8</b> , 1870 (1938).

Table 27. Catalytic Hydrogenation of Aromatic Nitro-Compounds.

Reaction	Catalyst	Observer
Hydrogenation of pyridine.	10% Pd asbestos.	Zelinsky and Borisoff: <i>Ber.</i> , <b>57</b> , 150-153 (1924).
Hydrogenation of pyridine under pressure.		Szadikow and Michailow: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>58</b> , 527-540 (1926).
Hydrogenation of pyridine derivatives containing basic groups, such as 3- or 5-halogen pyridine; 3-amino-pyridine obtained from 3-bromopyridine; T. 120-140°; time, 20 hrs.; yield, 75%.	$\text{CuSO}_4$ .	Chemische Fabrik von Heyden A.-G.: G.P. 586,879, Kl 12p, Oct. 27, 1933.
Hydrogenation of pyridine to piperidine (6-7 drops per min.); T. 130-150°; yield, 75%.	25 g. Ni dissolved in $\text{HNO}_3$ (2 : 1) in 500 cc. $\text{H}_2\text{O}$ to which is added 0.1 Pd solution in conc. $\text{HNO}_3$ plus 25 g. silicic acid gel.	Uchakov, Liwchitz and Jadanova: <i>Bull. soc. chim. (5)</i> , <b>2</b> , 573 (1935).

Table 28. Catalytic Hydrogenation of Nitro- Compounds.

Reaction	Catalyst	Observer
Hydrogenation of <i>o</i> -nitrotoluene to <i>o</i> -toluidine and toluene.	Ni formate.	G.P. 329,471, Kl 12o, Nov. 19, 1920.
Hydrogenation of xanthene to oxydicyclohexylmethane.	Ni oxide; alumina.	Ipatieff and Orlow: <i>Compt. rend.</i> , <b>183</b> , 973 (1926).
Hydrogenation of NO to hydroxylamine and ammonia in the presence of H <sub>2</sub> .	Platinized Pt; activated by dilution with HCl.	Butterworth and Partington: <i>Trans. Far. Soc.</i> , <b>26</b> , 144-147 (1930).
Hydrogenation of organic nitro-compounds in liquid phase, e.g., nitrobenzene, <i>p</i> -nitrophenol, <i>p</i> -nitrotoluene, <i>m</i> - and <i>p</i> -sodium nitrobenzoate; pressure, 14-17 atm.	Ni prepared from Ni formate.	Popow: <i>Anilinokrasochnaya Prom.</i> , <b>3</b> , 391-402 (1933).
Hydrogenation of nitroxylylene.	Ni [accelerated by methyl oleate, methyl palmitate and high-boiling paraffinic hydrocarbons (distilled medicinal paraffins)].	Green: <i>J. Soc. Chem. Ind.</i> , <b>52</b> , 172-173 (1933).
Hydrogenation of substituted nitrostyrols.	Pd on bone charcoal.	Reichert and Koch: <i>Ber.</i> , <b>273</b> , 265-274 (1935).
Hydrogenation of mononitrogenated alkyl benzene, e.g., 100 p. <i>o</i> -nitrotoluene and 75 parts Ni-kieselguhr catalyst (containing 25% active Ni), 5 parts H <sub>2</sub> O containing 0.09 NaOH; T. 80-100°; H <sub>2</sub> pressure, 400-500 lbs.; yield, 97-99% <i>o</i> -toluidine; NaOH may be replaced by Ba(OH) <sub>2</sub> , KOH, tetraethyl ammonium hydroxide; from <i>p</i> -nitrotoluene, <i>p</i> -toluidine is prepared; from nitroxylylene mixture obtained by nitrogenation of xylene, mixed xylydine is obtained.	Ni on kieselguhr carrier and small amounts of alkaline substances (up to 0.3% with respect to the nitro-compound).	Dupont (Henke and Benner): U.S.P. 2,131,734, Oct. 4, 1938.
Hydrogenation of nitroso-guanidine to amino-guanidine, using various solvents; T. 25°, 75° and 125°; the yields with nitroso-cpds. are greater than in the case of nitro-cpds.	Pt O <sub>2</sub> and Raney's Ni.	Lieber and Smith: <i>J. Am. Chem. Soc.</i> , <b>59</b> , 1834-35 (1937).

Table 29. Catalytic Hydrogenation of Nitriles.

Reaction	Catalyst	Observer
Hydrogenation of unsaturated nitriles to saturated nitriles.	Finely divided Ni on silica gel.	I. G. Farbenindustrie A.-G.: E.P. 255,884 (1916). F.P. 621,434 (1927).
Hydrogenation of saturated aliphatic, also aromatic nitriles to amines: $RCN + 2H_2 \rightarrow RCH_2NH_2$ (1) benzylicyanide to phenylethylamine; T. 70-100°; yield 18%. (2) $\alpha$ -naphthonitrile to primary (70%) and secondary (20%) amines.	Ni on silicic acid gel.	Sabatier and Senderens: <i>Compt. rend.</i> , <b>140</b> , 482 (1905). Frebault: <i>Compt. rend.</i> , <b>140</b> , 1036 (1905).
Hydrogenation of benzonitrile to benzylamine in alcohol, hydrochloric acid.	Pd charcoal.	Selden Co. (Jaeger): E.P. 304,640 (1929).
Hydrogenation of acetonitrile to ethylamine; open chains containing N <sub>2</sub> in an unsaturated form are hydrogenated.	Ni in the presence of NiSO <sub>4</sub> .	I. G. Farbenindustrie A.-G.: E.P. 307,000, Feb. 7, 1929.
Hydrogenation of nitriles of unsaturated fatty acids; T. 260°.	Cu carbonate, oxide, or hydroxide on bleaching earth, silica gel or charcoal.	I. G. Farbenindustrie A.-G. (Reppe and Hoffmann): G.P. 552,987 (1929).
Hydrogenation of crotonic acid nitrile to butyronitrile; T. 130° pressure, 30 atm. H <sub>2</sub> ; yield, 90%.	Cu-silicic acid on pumice, or Cu-silica gel.	

Table 29 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of ketone nitriles and their derivatives in the presence of elemental H.	Finely divided Pd.	Urluss: Leipzig (1931).
Hydrogenation of oxybenzonitriles and their methyl ethers; the yield of the aldehyde is increased in the presence of phenylhydrazine (10-25%), but hydrogenation is slowed down.	Ni.	Rupe and Brentano: <i>Helv. Chim. Acta</i> , 19, 588-596 (1936).
Hydrogenation of nitriles.		Komatus and Ishida: <i>Mem. Coll. Sci. Kyoto Imp. Univ. (A)</i> , 10, 217-228, 339-341 (1927).
Hydrogenation of nitriles and oximes.		Hartung: <i>J. Am. Chem. Soc.</i> , 50, 3370-3374 (1928).
Hydrogenation of nitriles under decreased pressure in vacuum.		Escourrou: <i>Bull. soc. chim.</i> (4), 45, 735-744 (1929).

Table 30. Catalytic Preparation of Nitriles.

Reaction	Catalyst	Observer
Preparation of nitriles.	Silicic acid gel.	Mitchell and Reid: <i>J. Am. Chem. Soc.</i> , 53, 321-330 (1931).
Preparation of nitriles from mandelic acid.		Brick: <i>J. Am. Chem. Soc.</i> , 55, 2593-2597 (1933).
Preparation of nitriles by passing EtCO <sub>2</sub> H and NH <sub>3</sub> through heated catalysts at the rate of 220-240 cc./min.; yield PrCN; (1) 95.5%; (2) 80.16% (3) 85.9%.	(1) Japanese acid clay. (2) SiO <sub>2</sub> gel. (3) Al <sub>2</sub> O <sub>3</sub> .	Abe: <i>Waseda Applied Chem. Soc. Bull.</i> , 19, 8-14 (1933).
Preparation of acetonitrile.	Japanese acid earth.	Kobagashi and Abe: <i>J. Soc. Chem. Ind. Japan</i> , 36, 42B-43B (1933).
Preparation of cyclic nitriles by catalytic cyanation of cyclic hydrocarbons and phenol ethers; catalyst added at the C : N bond of KC(:NH)CCl <sub>3</sub> and the resulting unstable assym. —KC(NH <sub>2</sub> )OK · CCl <sub>3</sub> decomposes spontaneously into CHCl <sub>3</sub> and a pseudoamide alkali cpd. KC(:NH)OH, which breaks down into KCN and KOH, the latter reacting with another molecule of KC(:NH)CCl <sub>3</sub> (nucleus condensation of cyclic cpds. with CCl <sub>3</sub> CN has been perfected).	KOH.	Houben and Fischer: <i>Ber.</i> , 66B, 339-349 (1933).

Table 31. Catalytic Hydrogenation of Nitrobenzene (Industrial Process).

Reaction	Catalyst	Observer
Hydrogenation of nitrobenzene to aniline.	Pd.	Kolbe and Saytzeff: <i>J. prakt. Chem.</i> , 4, 418 (1871).
Hydrogenation of nitrobenzene to aniline.		Sabatier and Senderens: <i>Compt. rend.</i> , 133, 321 (1901); 135, 226 (1902).
Hydrogenation of nitrobenzene to aniline.		Paal and Amberger: <i>Ber.</i> , 38, 1406 (1906).
Hydrogenation of nitrobenzene to aniline.	Ag or Au or mixtures of both.	Badische Anilin- und Soda Fabrik: G.P. 263,396 (1912).
Hydrogenation of nitrobenzene to aniline.	Pd.	Paal: G.P. 298,193 (1913).
Hydrogenation of nitrobenzene to aniline.	Ni.	Farbenfabrik vorm Meister Lucius Bruning: G.P. 282,492 (1913).
Hydrogenation of nitrobenzene to aniline.	Cu.	Badische Anilin- und Soda Fabrik: G.P. 282,568 (1913). G.P. 328,339 (1914).
Hydrogenation of nitrobenzene to aniline.		Brochet: <i>Bull. soc. chim.</i> (4), 15, 554 (1914).
Hydrogenation of nitrobenzene to aniline.	Charcoal	<i>J. Soc. Chem. Ind.</i> , 40, 445-447 (1921).

Table 31 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of nitrobenzene to aniline.		Brown and Henke: <i>J. Phys. Chem.</i> , <b>26</b> , 161, 272, 324 (1922); <b>27</b> , 52, 715, 739 (1923).
Hydrogenation of nitrobenzene to aniline.	Ag or Au, Fe, Zn with $\text{Cr}_2\text{O}_3$ or $\text{MnO}_2$ .	Badische Anilin- und Soda Fabrik: G.P. 436,820 (1924).
Hydrogenation of nitrobenzene to aniline.	Metal catalyst precipitated from a solution of Me salts by $\text{SiO}_2$ .	I. G. Farbenindustrie A.-G.: E.P. 301,557, Dec. 27, 1928. F.P. 641,652, Aug. 8, 1928.
Hydrogenation of nitrobenzene to aniline; the $\text{PhNH}_2$ of exceptional purity is freed from $(\text{PhNi})_2$ by treatment with alkali; T. 240–250°; yield (optimum) 96.5%.	A mixture of Cu and 10% CaO prepared from nitrates heated for 3–4 hrs. at 350° and reduced for 12 hrs. at 300° in $\text{H}_2$ ; retains its high activity for 80 hrs.	Irlin: <i>Anilinokrasochnaya Prom.</i> , <b>3</b> , 68–76 (1933).
Hydrogenation of nitrobenzene to aniline.	Double chromite of $\text{NH}_3$ and Ni; 17,650 g. $\text{Ni}(\text{NO}_3)_2$ dissolved in 3 l. $\text{H}_2\text{O}$ mixed with a solution of 750 g. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in equal parts of $\text{H}_2\text{O}$ , heated to 90–100° for 30 min., filtered, ppt. washed, and dried at 400° and reduced for 12 hrs. in dry $\text{H}_2$ .	Dupont (Lazier): U.S.P. 1,964,000, June 26, 1934.
Hydrogenation of <i>p</i> -chloronitrobenzene to chloraniline; no nitrobenzene formed; N–O bond more readily broken and hydrogenated than C–Cl bond.	Ni.	Balandin and Titova: <i>Izvest. Akad. Nauk U.S.S.R.</i> , <b>2</b> , 229–231 (1934).
Hydrogenation of nitrobenzene to aniline in the presence of $\text{H}_2$ ; 1 l. $\text{H}_2$ /min. to 39 g. nitrobenzene/hr.; yield, almost theoretical; with catalyst (1), T. 105–110°; with catalyst (2), T. 300–350°.	Alloys: (1) $\text{Al}_3\text{Ni}$ , $\text{Al}_2\text{Ni}$ and $\text{AlNi}$ with 73% and 27% Ni, respectively; 300 g. Ni–Al. (2) 30% Cu + 70% Al, treated with NaOH, washed and subjected to a stream of $\text{H}_2$ at 350°; particle size, 4–5 mm.	Bag. Jegupow and Wolokitin: <i>Prom. Org. Khim.</i> , <b>2</b> , 141–144 (1936). Rita and Mazume: <i>Z. angew. Chem.</i> , <b>36</b> , 389–91 (1923). (Refer to C. 1924 II 405).

Table 32. Catalytic Hydrogenation of Various Organic Compounds.

Reaction	Catalyst	Observer
Hydrogenation of fenchone to fenchane.	Joint action of catalysts.	Ipatieff and Matow: <i>Ber.</i> , <b>45</b> , 3205 (1912).
Hydrogenation of benzene to cyclohexane; reversible reaction.	Ni.	Sabatier.
Hydrogenation of carbonic acid to formic acid to $\text{H}_2$ and $\text{CO}_2$ ; reversible reaction.	Pd.	Bredig and Carter: <i>Ber.</i> , <b>47</b> , 542 (1914). Bredig and Carter: <i>Chem.-Ztg.</i> , <b>72</b> , (1915).
Hydrogenation of quinoline to decahydroquinoline; T. 125°.	Ni-kieselguhr.	Adkins and Cramer: <i>J. Am. Chem. Soc.</i> , <b>52</b> , 1349 (1930).
Hydrogenation of carbazol to perhydrocarbazol: (1) carbazol and decahydronaphthalene to perhydrocarbazol; T. 160–170°; (2) 100 g. carbazol and 200 g. butanol T. 250°; pressure, 50–100 atm. $\text{H}_2$ ; carbazol, similar to naphthalene, decomposes at 350° to benzene and aniline.	Ni-silicic acid.	I. G. Farbenindustrie A.-G.: G.P. 514,822 (1931). G.P. 595,135 (1933).
Hydrogenation of the furane nucleus; almost quantitative yield of tetrahydrofuran c.p. 746 at 78.5–80.0°; $n_D^{20} = 1.4067$ .	Os on asbestos (80–82°).	Zelinsky and Schujkin: <i>Doklady, Akad. Nauk. U.R.S.S.</i> ; 60–65 (1933).
Hydrogenation of indol bases.		Braun and Bayer: <i>Ber.</i> , <b>56</b> , 387–393 (1923).

Table 32 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of: (1) indol to dihydroindol; (2) 100 parts 2-methylindol to 2,3-dihydro-2-methylindol; T. 220°; pressure, 200 atm. H <sub>2</sub> ; yield 90-95%.	Cu or Cu-containing; 4 parts CuO prepared from CuCO <sub>3</sub> or precipitated from the nitrates of Cu : Al : Ba = 1 : 1/10 : 1/100 by NaHCO <sub>3</sub> reduced with H <sub>2</sub> + N <sub>2</sub> at 180-200°.	I. G. Farbenindustrie A.-G. (Treppenhauer); G.P. 623,693, Kl 12p, Dec. 31, 1935. F.P. 792,064, Dec. 21, 1935.
Hydrogenation of furan (1) and silvane (2) into their tetrahydroderivatives; (1) T. 100-140°; (2) T. 120°.	Os and Pd catalysts may be replaced by an alloy of 27% Ni with 73% Al treated with 10% NaOH (stable and active hydrogenation catalyst).	Schuilkin and Bunina: <i>Zhur. Obshchei Khim.</i> , 8 (70), 669-73 (1938).
Hydrogenation of furan nucleus to $\alpha$ -oxy-compounds; T. 150°; propionyl chloride acting upon furan forms $\alpha$ -propionyl furan and this is converted into hydrazone; the latter decomposes into $\alpha$ -n-propyl furan; hydrogenation of this at 170° gives $\alpha$ -n-propyltetrahydro-furan; likewise acetyl chloride acts upon silvane to form $\alpha$ -methyl- $\alpha'$ -acetyl furan; by decomposition of the hydrazone, $\alpha$ -methyl- $\alpha'$ -ethyl furan is obtained, and this converted into the corresponding tetrahydro- derivative.	Pd-asbestos with small content of KOH. AlCl <sub>3</sub> . KOH and platinized kaolin. AlCl <sub>3</sub> .	Schuilkin, Schemasstine and Tscherkassowa: <i>Ibid.</i> , 8 (76), 674-79 (1938); refer also to Gilman and Calloway: (C. 1934 I 862).
Preparation of tetrahydrofuran.	AlCl <sub>3</sub> , ZnCl <sub>2</sub> , MgCl <sub>2</sub> , CaCl <sub>2</sub> , <i>p</i> -toluenesulfonic acid, oxalic acid, succinic or maleic anhydrides, CuSO <sub>4</sub> , KAl sulfate, K <sub>2</sub> S <sub>2</sub> O <sub>7</sub> , or active Al <sub>2</sub> O <sub>3</sub> .	I. G. Farbenindustrie A.-G.; E.P. 508,548, July 27, 1939.
Hydrogenation of $n$ -propyl and furyl carbinol.	PtO <sub>2</sub> .	Kondo and Takeda: <i>J. Pharm. Soc. Japan</i> , 55, 140-142 (1935).
Hydrogenation of furyl acrolein to $n$ -heptane; yield, 8-12%.	MoS <sub>2</sub> .	Orlow, Glinskich and Ignatowitsch: <i>Zhur. Priklad. Khim.</i> , 8, 1170-1175 (1935). Burdick and Adkins: <i>J. Am. Chem. Soc.</i> , 56, 438-42 (1934); (Refer to C. 1934 I 2281).
Hydrogenation of furyl ethyl carbinol to Decalin; T. 340°; initial pressure, 100 atm.	MoS <sub>2</sub> : NiO = 7 : 3. MoS <sub>2</sub> : CoS = 7 : 3.	
Hydrogenation of dipropyl ketene to Decalin; T. 345°; maximum pressure, 194 atm.; (gave 37.6% heptane).	MoS <sub>2</sub> : CoO = 7 : 3.	
Hydrogenation of cinnamic aldehyde and citronellal.	Usual catalysts.	Delépine and Hanegraaff: <i>Bull. soc. chim.</i> (5), 4, 2087-2093 (1937).
Preparation of tetrahydrofuran; vapors of 1,4-butylene glycol are led over agents, which cause water to split off; T. 220-450°; yield almost 100%.	Cr <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , CaCl <sub>2</sub> , as well as Ca-, Sr-, Ag-, and Hg-phosphates.	I. G. Farbenindustrie A.-G.; E.P. 506,674, June 29, 1939.
Hydrogenation of sugar to polyvalent alcohol (glycol); T. 200-300°; pressure greater than 70 atm.; e.g., 150 g. glucose, 75 g. water, 10 g. CaCO <sub>3</sub> and 15 g. Ni treated with H <sub>2</sub> ; T. 250°; pressure 170 atm.; yield, 24 g. glycerin and 35 g. of a mixture of ethylene and propylene; the impurities obtained from glycerin are removed by solvents such as CHCl <sub>3</sub> , (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O, or CCl <sub>4</sub> .	Ni, Co, and a weak alkali buffer solution; CaCO <sub>3</sub> with 10% alcohol.	Dupont: E.P. 430,576, July 18, 1935.



Table 32 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of furfural to furfuryl alcohol; temp. not higher than 200°; pressure, 100 atm.	Ni chromite; Cu chromite loses its activity very rapidly.	Roberti: <i>Ann. chim. applicata</i> , <b>25</b> , 530-540 (1935).
Hydrogenation of furfural to furfuryl alcohol; of ethyl laurate (ester) to dodecyl alcohol; likewise, dehydrogenation of octadecandiol, oxystearin, cyclohexanol, methylcyclohexanol, decahydro- $\alpha$ -naphthol.	Chromites of Cu, Ag, Zn, Cd obtained by glowing the double chromates of these metals with nitrogen bases ( $\text{NH}_4^-$ ) and followed by extraction with about 10% $\text{NH}_3$ .	Dupont (Salzberg): U.S.P. 2,129,507, Sept. 6, 1938
Preparation of $n$ -heptane: (1) by hydrogenation of mixtures of $\alpha$ -, $\beta$ - and $\gamma$ -heptenes (waste products obtained in the preparation of heptene carboxylic acid in an autoclave); initial pressure, 80-85 atm. $\text{H}_2$ ; (2) by hydrogenation of oenanthylic acid or its esters obtained from oenanthal; T. 350-370°; initial pressure, 108 atm. $\text{H}_2$ (industrial process).	Ni.  Cu—Cr.	Petrow and Andrejew: <i>Prom. Org. Khim.</i> , <b>2</b> , 455-457 (1936).
Hydrogenation reactions.	Catalyst prepared by precipitating a mixture of metals as chromites with $(\text{NH}_4)_2\text{CrO}_4$ , e.g., 62 g. $\text{Cd}(\text{NO}_3)_2$ in 150 cc. $\text{H}_2\text{O}$ added to 574 g. $\text{ZnSO}_4$ in 2 l. $\text{H}_2\text{O}$ added to 305 g. $(\text{NH}_4)_2\text{CrO}_4$ in 2.2 l. $\text{H}_2\text{O}$ (neutral); metals obtained by heating: (1) an oxide (Mg, Zn, Mn) not reduced for many hours at 400° in $\text{H}_2$ ; (2) an oxide (Ag, Cu, Cd, Pb, Hg, Sn, Bi, Fe, Co, Ni) which is reduced under identical conditions.	Dupont (Lazier): U.S.P. 2,066,153, Dec. 29, 1936
Destructive hydrogenation of propane; T. 138°; decomposition by $\text{D}_2$ proceeds slower than by $\text{H}_2$ : $\text{C}_3\text{H}_8 + \text{H}_2 = \text{CH}_4 + \text{C}_2\text{H}_6$ and the ethane formed is converted further into $\text{CH}_4$ : $\text{C}_2\text{H}_6 + \text{H}_2 = 2\text{CH}_4$ ; activation energy 34 cal.; in hydrogenation of $\text{C}_2\text{H}_4$ splitting of the C—C bond is not observed even at 138°; hydrogenation of $\text{C}_2\text{H}_4$ with $\text{D}_2$ at -80 to 65° completed in 15 min.; T. 0°; time, about 1½ hrs.; the amount of $\text{H}_2$ and saturated hydrocarbons adsorbed is very small; an exchange between $\text{D}_2$ and $\text{C}_2\text{H}_4$ and $\text{H}_2$ and $\text{D}_2$ takes place and a C—D bond is obtained; reaction between $\text{H}_2$ and $\text{C}_2\text{H}_4$ , very complex, in which $\text{H}_2$ exchange and polymerization to $\text{C}_6$ and high molecular weight hydrocarbons occur; absence of $\text{CH}_4$ and propane in reaction products indicates stability of C—C bond.	Ni—kieselguhr $\text{Ni—kieselguhr} + \text{H}_2\text{O} + \text{D}_2 =$ $\text{Ni—kieselguhr} \text{D}_2\text{O} + \text{H}_2$	Morikawa, Trenner and Taylor: <i>J. Am. Chem. Soc.</i> , <b>59</b> , 1103-1111 (1937).
	Ni.	
	Cu (obtained by alternating reduction and oxidation of granulated CuO).	
Hydrogenation of ethane; $\text{H}_2$ : $\text{C}_2\text{H}_6$ was varied; T. 184-280°; initial pressure of $\text{C}_2\text{H}_6$ , 73 mm.; activation energies between 30 and 34 kcal.; the reaction over Co catalysts similar to that over Ni is slowed down, but to a smaller extent, by $\text{H}_2$ ; dependence of velocity on $\text{H}_2$ conc. changes thereby with the nature of the second component of the catalyst between -0.5 and -1.6.	(1) Co—Th—Cu on kieselguhr; (2) 4Co—Mg Co is less active than Ni, but much more active than Cu; the Co—Mg catalysts are more active than Th-containing catalysts; their activity increases with increasing Co content.	Taylor, E. H., and Taylor, H.: <i>J. Am. Chem. Soc.</i> , <b>61</b> , 503- (1939); refer also to Morikawa, Benedict and Taylor: (Refer to C. 1937 II 1972) and Taylor and Joris: (Refer to C. 1937 II 3713).

Table 32 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of petroleum distillate after removal of $\text{SO}_2$ ; T. $530^\circ$ ; pressure 210 atm.; followed by sulfonation at $65^\circ$ ; sulfonic acid melted at $350^\circ$ with KOH or NaOH or chlorinated or heated with aqueous NaOH; T. $340\text{--}380^\circ$ ; pressure 140–280 atm.; phenols obtained.	Mo oxide and Mo sulfide.	Standard Oil Development Co.: E.P. 477,015, Jan. 13, 1938.
Hydrogenation of abietyl cpds. in liquid phase at high temp. and pressure; at first abietyl alcohol is heated with the simultaneous passing of $\text{H}_2$ ; a temp. of $100^\circ$ and a pressure of 15 atm. are required to hydrogenate one double bond in an abietyl cpd.; a temp. of $210\text{--}230^\circ$ and a pressure of 57–70 atm. are required to hydrogenate two double bonds in an abietyl cpd.	Al—Ni alloy + Cu, Zr, Ce or Co as activators; the alloy is broken into pieces which pass through a 2-mesh sieve and are treated with $\text{H}_2$ or an alkaline solution, such as $\text{Na}_2\text{CO}_3$ or NaOH; catalyst regenerated by treatment with NaOH; catalyst also may be used in the hydrogenation of phenol, naphthalene, nitrobenzene, furfural, pyridine, pinene and dipentene.	Hercules Powder Co. (Byrkit): U.S.P. 2,094,117, Sept. 28, 1937.
Hydrogenation, oxidation or $\text{H}_2$ treatment of carbohydrates; sucrose, dextrose treated with $\text{H}_2$ converted into propylene glycol, glycerin and a non-volatile liquid; glycerin gives at $250^\circ$ chiefly acetol; methanol and air to HCHO; soy-bean oil treated with $\text{H}_2$ gives a liquid with iodine number 124.4.	Cu—Al (the oxides are heated to $750\text{--}1100^\circ$ until the catalyst acquires a cocoa color and becomes insoluble in acids; it may be activated with $\text{H}_2$ at $200\text{--}350^\circ$ ; alkalis act as promoters (0.1–10.0%).	Association of American Soap and Glycerin Producers, Inc.: F.P. 825,688, March 10, 1938.
Hydrogenation of diphenyl fulvene in alcohol, ether, acetic acid and cyclohexanone; hydrogenation proceeds stepwise and the selectivity of $\text{H}_2$ addition is greatest when working with Pd black in alcohol; $\text{H}_2$ is added, without an apparent selectivity, to the double bonds of the ring and then very slowly to the semi-cyclic double bond.	Pt and Pd black.	Kasanski and Tatewossjan: <i>Zhur. Obshchei Khim.</i> , 8 (70), 1428–37 (1938).
Hydrogenation of duroquinone to durohydroquinone (2,3,5,6-tetramethyl-1,4-dioxybenzene); 20 g. duroquinone dissolved in 1500 cc. alcohol shaken with $\text{H}_2$ in the presence of a catalyst at room temp. for 40 min.; 94% yield; as solvents, glacial acetic acid, ether, or toluene, may be used.	0.5 g. 10% Pd-charcoal; Pt oxide or Raney's Ni.	Merck Chemische Fabrik (Jung): G.P. 676,198, Kl 12g. May 30, 1939.
Hydrogenation of naphthenic acid derivatives into the corresponding primary alcohols, e.g., naphthenic acid ethyl ester (obtained by esterification of a naphthenic acid fraction from Russian petroleum at $140\text{--}180^\circ$ and 20 mm. pressure) is treated with $\text{H}_2$ over the catalyst in an autoclave for $9\frac{1}{2}$ hours at 3000 lbs. per sq.in. pressure at $260\text{--}270^\circ$ .	Ba containing Cu chromite.	Dupont: U.S.P. 2,114,717, April 19, 1938.
Hydrogenation of naphthenic acids obtained from mineral oil sludge to naphthenyl alcohols; these may be converted by means of NaOH and $\text{CS}_2$ in xanthogenate which are used in oil flotation processes, or as vulcanization accelerators, etc.; by treating these alcohols with $\text{POCl}_3$ naphthenyl-phosphate is obtained which is suitable for softening in the preparation of cellulose derivatives.	Usual catalysts.	Wunsch: U.S.P. 2,120,537, June 14, 1938.

Table 32 (Continued).

Reaction	Catalyst	Observer
Hydrogenation and dehydrogenation of carboxylic acids, their esters, or anhydrides; T. 300–400°; pressure, 1500–3000 lbs./sq.in.; yield, 85% corresponding alcohols from a synthetic fatty acid mixture of $C_{18}H_{36}$ with only 1.2% hydrocarbons.	Metals of the Fe group, as well as oxides or chromites with addition of chromites of metals such as Cd, Sn, Hg, Ti, Pb, and Bi; especially suitable are Cd–Ni chromite, Co–Cd, as well as their chromites; Cd–Co–Ni chromite, Fe–Cd, as well as their chromites, and Ni–Cd chromite; Ni–Co–Cd chromite, ratio 45 : 45 : 10.	Dupont (Arnold and Lazier): U.S.P. 2,116,552, May 10, 1938.
Hydrogenation of octenes to octanes (octene obtained by polymerization of butylene); T. under 200°; low pressure (below 4 atm.); (Shell Co. developed this method); octane obtained has octane number around 98 (ASTM Method); small content in unsaturated hydrocarbons, S and resin; its vapor pressure is low corresponding to the high critical point of octanes.	Finely divided Ni.	Otin and Dima: <i>Refiner and Natural Gasoline Mfr.</i> , 17, 283–288 (1938).
Hydrogenation of octenes (obtained by polymerizing butylene and isobutylene with $H_2SO_4$ in gaseous phase to octanes); T. 180–190°; pressure, 1–4 atm.; yield, 99%; gases freed from S before hydrogenation; after a superficial purification, they are led over the Ni catalyst with exhausted hydrogenation power; S content reduced from 0.002 to 0.0005%; $H_2$ prepared by cracking natural gas, ammonia dissociation, or electrolysis.	Ni precipitated on porcelain; catalyst, when partially exhausted, reactivated by $O_2$ in air, followed by reduction in a stream of $H_2$ ; catalyst placed in a group of tubes surrounded by cooling liquid of definite temp.	Turner and Mayer: <i>Oil and Gas J.</i> , 37 (2), 50–55 (1938).
Hydrogenation of 2,5-dimethyl-2,5-dioxihexine-3 dissolved in a volatile solvent, such as water or methanol; T. 73–75°F.; yield of ethylene cpds., 98.5%.	Ni activated with a trace of NaOH (Raney's type).	Carbide and Carbon Chemicals Corporation (Vaughn): U.S.P. 2,157,365, May 9, 1939.

Table 33. Catalytic Hydrogenation of Fluorene and Retene.

Reaction	Catalyst	Observer
Hydrogenation of Retene (1-methyl-4-isopropylphenanthrene).	Phosphorus.	Bamberger and Hooker: <i>Ann. chim.</i> , 229, 102 (1889). Bamberger and Hooker: <i>Ber.</i> , 22, 635 (1889).
Hydrogenation of fluorene and Retene; Retene when completely hydrogenated is identical with a hydrocarbon (tichbelite) found in peat; the highest hydrogenation product of Retene is dodecahydoretene, $C_{18}H_{18}$ .	NiO.	Ipatieff: <i>Ber.</i> , 42, 2092 (1910). Metzger: <i>Ber.</i> , 40, 1289 (1907). Schmidt and Fischer: <i>Ber.</i> , 41, 4227 (1909). Liebermann and Spiegel: <i>Ber.</i> , 22, 780 (1889).

Table 34. Catalytic Hydrogenation of Heterocyclic Compounds (Pyrrole Derivatives).

Reaction	Catalyst	Observer
Hydrogenation of the homologs of pyrrole and dehydrogenation of their tetrahydro-derivatives.	Pd asbestos.	Jurjew and Scheujan: <i>Zhur. Obshchei Khim.</i> , 4 (66), 1258–1261 (1935).
Hydrogenation of pyrrole derivatives; T. 180°; pyrrole, more resistant to action of $H_2$ than many other unsaturated ring cpds. (1) 2,3,4,5-alkyl-pyrrole to pyrrolidine; T. 200–250°;	Ni.  Cu— $Cr_2O_3$ .	Signaigo and Adkins: <i>J. Am. Chem. Soc.</i> , 58, 709–716 (1936).  Connor, Folkers and Adkins: <i>Ibid.</i> , 54, 1138–45 (1932); (Refer to C. 1932 I 2565).

Table 34 (Continued).

Reaction	Catalyst	Observer
(2) <i>n</i> -aryl or <i>n</i> -carbathoxy-pyrrole between room temp. and 180°; hydrogenation of carbathoxypyrroles at higher temp. leads in part to the formation of methylpyrroles.	Raney's Ni.	Adkins and Covert: <i>Ibid.</i> , <b>54</b> , 4116-17 (1932); (Refer to C. 1933 I 179).
Hydrogenation of acetylenyl-divinyl magnesium halogenide ( $\text{CH}_2=\text{CH} \cdot \text{CH}=\text{CH}-\text{C} \equiv \text{CMgBr}$ ) treated with aldehydes or ketones to form unsaturated alcohols having at least one triple (acetylene) bond and two double (ethylene) bonds; to an ether solution of ethylene magnesium bromide stirred with 1.5 times the amount of a mixture containing 50 g. divinylacetylene and acetylenyldivinyl in 100 cc. ether is added, after 12 hrs. standing, 35 g. acetone; after another 12 hrs. it is treated with moistened and acidified ether, the product extracted with ether and fractionated in vacuum.	Hydrogenation catalyst.	Salkind and Sokis: Russ. P. 51,905, Oct. 31, 1937.
Hydrogenation of pyrridyl-pyrrole derivatives under pressure; pyrridyl-pyrrole derivatives of the pyrridine ring are more readily hydrogenated than the pyrrole ring, as confirmed by compounds I to VI; it is claimed by these investigators that the ease of hydrogenation in the pyrrole nucleus depends on its substitutes, <i>e.g.</i> , the methyl group has very little influence; the oxy-ethyl group, as well as the ethyl group, may be hydrogenated, while the acetyl or carbathoxy-groups are difficult or impossible to hydrogenate.		Ochiai, Tsuda and Ykuma: <i>Ber.</i> , <b>69</b> , 2238-2242 (1936). Overhoff and Wibaut: <i>Rec. trav. chim.</i> , <b>50</b> , 957-80 (1931); (Refer to C. 1931 II 3483).

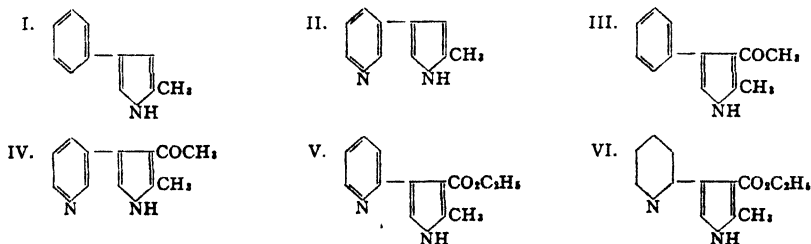


Table 35. Catalytic Hydrogenation of Aromatic Compounds.

Reaction	Catalyst	Observer
Hydrogenation of aromatic cpds.	Ni prepared by heating above 350° incapable of hydrogenating the aromatic nucleus.	Darzeus: <i>Compt. rend.</i> , <b>139</b> , 869 (1904). Brunel: <i>Ann. chim. phys.</i> (8), <b>6</b> , 205 (1903).
Hydrogenation of aromatic cpds. with an ethylene bond.	CuO.	Ipatieff: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>41</b> , 760 (1909).
Hydrogenation of the nucleus of aromatic and fatty aromatic aldehydes in the form of their acetates.		Sigmund: <i>Ber.</i> , <b>48</b> (1915). Adams and Adkins: <i>J. Am. Chem. Soc.</i> , <b>47</b> , 1358-1367 (1925).
Hydrogenation of diphenyl; T. below 160°; pressure, 90-100 atm.	Ni—Al <sub>2</sub> O <sub>3</sub> .	Zelinsky and Pawlow: <i>Ber.</i> , <b>57</b> , 669-71 (1924). (Refer to C. 1924 I 2407).
Hydrogenation of aromatic cpds.	Pt.	Willstätter and Jaquet: <i>Ber.</i> , <b>51</b> , 767-749 (1918).

Table 35 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of aromatic cpds. in presence of $O_2$ .	Pt.	Willstätter and Waldschmidt: <i>Ber.</i> , <b>54</b> , 113-138 (1921).
Hydrogenation of aromatic hydrocarbons.	NiO and CuO.	Anilin Fabrikation A.-G.: G.P. 383,540, Kl 12o, Gr 25, Feb. 19, 1924.
Hydrogenation of salts of aromatic acids under pressure; T. up to 300°.	NiO.	Ipatieff and Rasuwajew: <i>Ber.</i> , <b>59</b> , 2028 (1926).
Hydrogenation of aromatic hydrocarbons.	A contact mass containing a permutogenetic body and at least one catalytically-acting, but not base-exchanging component.	Selden Co. (Jaeger): E.P. 306,803, April 24, 1929. Can. P. 296,913, Jan. 21, 1930.
Hydrogenation of aromatic to high-boiling hydrocarbons; a mixture of CO and $H_2$ is converted with addition of alkali, such as Na and Li, at 270-350° under high pressure into low-boiling liquid hydrocarbons, which in turn are converted under pressure and at a temp. of less than 250° in the presence of anhydrous inorganic halide compounds, such as $AlCl_3$ , into high-boiling hydrocarbons.	Catalysts from the 8th group; $AlCl_3$ .	I. G. Farbenindustrie A.-G. (Wietzel, Speer and Kaepfer): U.S.P. 1,192,288, March 31, 1931. E.P. 345,334, April 16, 1931.
Hydrogenation of aromatic hydrocarbons at high pressure.	Ni on kieselguhr.	Shoorel, Tulleners and Waterman: <i>J. Inst. Petroleum Tech.</i> , <b>18</b> , 179-182 (1932).
Hydrogenation of aromatic hydrocarbons and substitutes with double bonds.	$NaNH_2$ , instead of NaH, used; catalytic action greatest at a temp. at which Na adsorbs $H_2$ in autoclave; when changed into a catalyst, serves for the cracking of dibenzyl polystyrol.	Hugel and Fries: <i>Bull. soc. chim.</i> (4), 1042-1047 (1931).
Hydrogenation of hydrocarbons under pressure; 30% saturated or aromatic hydrocarbons in vapor phase are added before heating to the reaction temp.; precautions taken to avoid tarring of the catalyst.		I. G. Farbenindustrie A.-G.: F.P. 717,673, Jan. 12, 1932.
Hydrogenation of styrol to diphenylethanaphthalene to tetrahydronaphthalene or diphenylbutadiene to diphenylbutane.	NaH.	Hugel and Gidaly: <i>Bull. soc. chim.</i> (4), <b>51</b> , 639-644 (1932).
Hydrogenation of benzal fluorene and anisal fluorene.		
Preparation of xanthene derivatives of theophylline and paraxanthene from their 8-chloro-derivatives by hydrogenating in an aqueous alkaline solution at 100° under 30 to 40 atm. pressure.	0.1% hydrogenation catalyst.	Boehringer und Sohn A.-G.: G.P. 582,435, Aug. 15, 1933.
Destructive hydrogenation of aromatic hydrocarbons; T. 460°; pressure, 50-250 atm. $H_2$ ; hydrogenation velocity expressed by the equation: $\log K = 6.87 + \log p_{H_2} / 273 (T. - 558/T)$ , where $K$ is the amount of toluene in g.; $H_2$ partial pressure in $p_{H_2}$ atm., and $T^\circ K.$ , the reaction temp.; in the temp. interval 400-460°, the apparent activation energy is constant and equals 23-100 k cal.; reaction velocities in the hydrogenation of aromatic hydrocarbons, varying in structure, at 420° and $H_2 = 100$ atm., gave the following sequence: benzene less than toluene less than xylene less than pseudocumol less than naphthalene.	$MoS_2$ , 1 kg.	Altman and Nemsow: <i>Acta Physicochim. U.R.S.S.</i> , <b>1</b> , 429-448 (1934).
Hydrogenation of aromatic cpds. at close to their decomposition temp.	$MoO_3$ , NiO- $Al_2O_3$ , CuO- $Al_2O_3$ , $MoO_3$ - $Al_2O_3$ , $Al_2O_3$ .	Ipatieff: <i>J. Am. Chem. Soc.</i> , <b>55</b> , 3696 (1933).
Hydrogenation of aromatic cpds. (benzene) under high pressure.	NiO.	Tanaka, Kobayashi, Endo and Fujita: <i>J. Soc. Chem. Ind. Japan</i> , <b>37</b> , 538B-539B (1934).

Table 35 (Continued).

Reaction	Catalyst	Observer
Destructive hydrogenation of aromatic cpds.	MoS <sub>2</sub> .	Altmann and Nemzow: <i>Zhur. Fiz. Khim.</i> , 6, 221-233 (1935).
Preparation of dihydromorphine from morphine, particularly its phenolic ethers, e.g., dehydrogenation of codeine hydrochloride solution to codeine; T. 195°F.; yield, 75-85%.	Pd.	Knoll A.-G.: G.P. 607,931, Jan. 11, 1935.
Hydrogenation of liquid hydrocarbons (low-, medium, or high-boiling fractions from benzene); T. 100-275°; pressure, 20-500 atm.; only diolefins, resins and asphalts are hydrogenated; at higher temp., aromatizing hydrogenation or cracking takes place.	Oxides, phosphides, nitrides, sulfides of metals of the 2nd to 8th groups, e.g., Mo, W, Cr, V, Mn, Co, Ni, Fe, Zn, Rh, U, Sn.	International Hydrogenation Patents Co., Ltd.: E.P. 424,531, March 21, 1935.
Hydrogenation of aromatic and naphthenic hydrocarbons, especially from oil extracts with selective solvents, under pressure; this reaction is so conducted as to prevent precipitation of solid substances by eliminating from the hydrogenation products a middle fraction at 213-224°, cooling and separating the solid substance by filtering; the liquid part of the hydrogenation products boiling above 224° is recirculated for repeated hydrogenation.		International Hydrogenation Patents Co., Ltd.: F.P. 828,557, May 20, 1938.
Hydrogenation of diphenyl to dicyclohexyl; T. below 160°; initial pressure, 90-100 atm.; heated over 25 parts AlCl <sub>3</sub> with stirring at 160-290° gives 32% hexamethylene cpds., chiefly dimethylcyclohexane [determined by dehydrogenation of the corresponding aromatic cpds. according to Zelinsky (Refer to C. 1911 II 1794)], 12.4% pentamethylene cpds. and 55.6% hydrocarbons of the methane series; comparing the results obtained with results of similar experiments using diphenyl and AlCl <sub>3</sub> , it has been found that as a result of greater stability of the benzene ring the separation of both rings for diphenyl is much easier than for dicyclohexyl, the latter suffering chiefly a break in the ring with the formation of alkylcyclohexanes.	Ni-Al <sub>2</sub> O <sub>3</sub> .	Jurjew, Lewina and Kudrjawzew: <i>Zhur. Obshchei Khim.</i> , 6 (68) 1500-1505 (1936). Jurjew, Lewina and Kudrjawzew: (Refer to C. 1924 I 2407).
Hydrogenation or dehydrogenation under pressure, also splitting off of the OH groups from phenols.	Charcoal extracts heated between 600-1000° in the presence of water vapor; likewise impregnated with ZnCl <sub>2</sub> , H <sub>3</sub> PO <sub>4</sub> , or HCl.	International Hydrogenation Patents Co., Ltd.: F.P. 820,633, Nov. 16, 1937.
Catalytic hydrogenation of organic compounds (quinone, benzoquinone, etc.) with CO; CO precipitates Pd from Pd salt solutions:	Pd in acid (HCl) solution.	Neunhoeffer and Pelz: <i>Ber.</i> , 72, 433-39 (1939).
Pd + R + 2HCl → RH <sub>2</sub> + PdCl <sub>2</sub> (PdCl <sub>2</sub> is reduced to metal through H <sub>2</sub> ); the CO hydrogenation cannot be applied to some cpds. hydrogenated with H <sub>2</sub> , e.g., nitrobenzene and cyclohexene are not hydrogenated; nitrobenzoic acid hydrogenates only slowly to amino-benzoic acid; CO <sub>2</sub> inhibits hydrogenation and must be continuously removed during the reaction; it is assumed that "active hydrogen" is monoatomic and is added as such to the acceptor; one mol of H <sub>2</sub> acts upon the radical so formed in such a way that one atom is added to the radical and a second atom to the catalyst, whereby the latter is converted into its initial state.		

Table 36. Catalytic Hydrogenation of Naphthalene (Industrial Process).

Reaction	Catalyst	Observer
Hydrogenation of naphthalene; reaction temp. decreased almost twice by Ni.	NiO + Al <sub>2</sub> O <sub>3</sub> .	Ipatieff and Matow: <i>Ber.</i> , 45, 3205 (1912).
Hydrogenation of naphthalene derivatives (acenaphthene).	Na, NH <sub>3</sub> .	Lebeau and Picon: <i>J. pharm. chim.</i> (7), 10, 97-100 (1914).
Hydrogenation of naphthalene to Tetralin in the presence of 2 mols H <sub>2</sub> .	Ni + Cu.	Tetralin G.m.b.H. (Schroeter): G.P. 299,012 (1916). G.P. 299,013 (1916).
Hydrogenation of naphthalene to tetra- and decahydronaphthalene on an industrial scale; T. 170-200°; pressure, 10-15 atm.	Ni on kieselguhr (may be used for the hydrogenation of benzene hydrocarbons); it is recommended substituting a Ni catalyst during hydrogenation; 20% NiO on pieces of ton (may be used twice); 20% NiO on kieselguhr (may be used three times).	Tetralin G.m.b.H. (Schroeter): E.P. 147,476 (1916). E.P. 147,488 (1916). Tetralin G.m.b.H. (Schroeter): <i>Ann.</i> , 226, 1 (1922). Waterman, Clausen and Tulleners: <i>Rec. trav. chim.</i> , 53, 821 (1934). Brochet and Schmitz: U.S.P. 1,896,282 (1933).

Table 36 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of naphthalene to tetrahydronaphthalene; a diphenyl, $(C_6H_5)_2$ is formed; naphthalene at ordinary pressure does not hydrogenate over NaH at 300°; under high pressure, it is hydrogenated between 250–350° only up to tetrahydronaphthalene; independent of the initial pressure.	NaH.	Farbenfabriken vorm. Friederich Bayer & Co.: G.P. 306,724, Kl 12o, Oct. 7, 1915.
Hydrogenation of naphthalene to (1) <i>trans</i> -decahydronaphthalene and (2) <i>cis</i> -decahydronaphthalene, exclusively.	(1) Ni. (2) Pt.	Willstätter: <i>Sitzber. Akad. Wiss. Wien</i> , <b>57B</b> , 683 (1924).
Hydrogenation of naphthalene to benzene hydrocarbons under pressure; T. 450–480°; time, 25–30 hrs.; the hydrogenated nucleus is split into benzene hydrocarbons.	Equal parts NiO and Al <sub>2</sub> O <sub>3</sub> .	Ipatieff and Klukwin: <i>Ber.</i> , <b>58</b> , 1 (1925).
Hydrogenation of naphthalene to Tetralin exclusively.	Ni.	Lush: <i>J. Soc. Chem. Ind.</i> , <b>46</b> , 454–456 (1927).
Hydrogenation of commercial naphthalene.	Alloys NaK or NaK <sub>2</sub> ; also with Ni.	Guyot: <i>Chimie &amp; industrie</i> , <b>19</b> , 410 (1928).
Hydrogenation of naphthalene to benzene hydrocarbons; T. 450°.	Melted Fe <sub>2</sub> O <sub>3</sub> activated with Al <sub>2</sub> O <sub>3</sub> and small amounts of alkali; reduced with H <sub>2</sub> at 400°.	I. G. Farbenindustrie A.-G. (Schmidt, Ufer and Krönig): F.P. 612,908 (1930). Swiss P. 127,689. Swiss P. 127,690. Swiss P. 127,691.
Hydrogenation of naphthalene.	Active charcoal or brown coal with MoO <sub>3</sub> or Mo sulfide.	N. V. de Bataafsche Petroleum Mij: E.P. 349,470 (1931).
Hydrogenation of naphthalene and benzene to benzene under pressure.	Active charcoal impregnated with ammonium molybdate solution and H <sub>2</sub> S or ammonium vanadate.	International Hydrogenation Patents Co., Ltd.: F.P. 728,287, July 4, 1932. E.P. 379,587, Sept. 22, 1932.
Hydrogenation of naphthalene to Tetralin and Dekalin; T. 340–440°.	Mo + W + difficultly reducible metal oxides.	Deutsche Gold und Silber Scheideanstalt (Roessler): F.P. 40,849, Sept. 7, 1932. add to F.P. 683,067. I. G. Farbenindustrie A.-G.: F.P. 734,879, Oct. 29, 1932.
Hydrogenation of naphthalene to benzene hydrocarbons; yield, 50%.	Fe, Co, Ni and especially their oxides.	Deutsche Gold und Silber Scheideanstalt (Roessler): F.P. 40,849, Sept. 7, 1932.
Hydrogenation of naphthalene; T. 180–200°; pressure, 15–20 atm.; best yield with catalyst as indicated.*	Ni (from the formate, hydroxide, or nitrate or in combination with potassium aluminate); Ni + Cu formate Ni + Al formate Ni + Fe formate *37% Ni + 63% Na aluminat.	Popov: <i>Ukrain. Khem. Zhur.</i> , 41–56 (1932).
Hydrogenation of crude naphthalene to Tetralin; T. 325°; time, 3 hrs.; pressure, 100 atm.; theoretical yield; naphthalene pretreated with 3% of 90% H <sub>2</sub> SO <sub>4</sub> distilled under 20–30 mm. pressure.	20% Ni precipitated on silica gel or kaolin (clarite); used twice on kaolin 7 times on fluoridin 8 times on tonsil 3 times on kieselsguhr 6 times on magnesite 4 times on precipitated and glowd SiO <sub>2</sub> 27 times on silica gel.	Brochet and Schmitz: U.S.P. 1,896,282, Feb. 7, 1933.
Hydrogenation of naphthalene to Tetralin; T. 350°; time, 2 hrs. (400°); pressure, 100 atm. H <sub>2</sub> ; yield, 94.5%.	(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> ; MoS <sub>3</sub> (increases the yield of Tetralin to 91% at 350°).	Hall: <i>Fuel</i> , <b>12</b> , 76–93 (1933).

Table 36 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of naphthalene to Tetralin and Dekalin; T. 400°; pressure, 200 atm.; <i>trans</i> -Dekalin formed at 350°; <i>cis</i> -Dekalin at 75°; the isomer of <i>trans</i> -Dekalin formed best at 360-70°; without a catalyst, no isomerization takes place; Dekalin splits above 400°; accelerated passage velocity slows down the conversion of Tetralin in high-pressure hydrogenation; in a continuous process, it may be subjected to higher temp. (360-370°) instead of longer contact time at lower temp.	MoS <sub>2</sub> .	Prokopetz: <i>Zhur. Priklad. Khim.</i> , 7, 159-169 (1934). Prokopetz: <i>Khim. Tverdogo Topliva</i> , 5, 832-839 (1934). Hall: <i>Fuel</i> , 12, 76-93 (1933).
Hydrogenation of naphthalene to Tetralin (very little Dekalin formed); T. 475°; resists well the poisoning effect of H <sub>2</sub> S in commercial naphthalene; at 520°, three times more naphthalene converted with molybdic acid than with MoS <sub>2</sub> catalyst.	Fe iodide (better than the chlorides of Al or Fe, as well as alkaline-earth metals); Mo and W oxides or sulfides (better action from oxides); molybdic acid, best catalyst; WS <sub>2</sub> , less active.	Varga: <i>Math. naturw. Anz. ungar. Akad. Wiss.</i> , 50, 408-426 (1934).
Hydrogenation of naphthalene to Tetralin and Dekalin and of benzene and phenol to cyclohexane, as well as cyclohexanol.	Ni splinters.	Technical Research Works, Ltd. (London); G.P. 595,615, Kl 12o, April 24, 1934.
Destructive hydrogenation of naphthalene to liquid hydrocarbons; T. above 500°; pressure, 100 atm. H <sub>2</sub> ; yield, 70-75%; the destructive hydrogenation of Tetralin proceeds more readily.	2% MoS <sub>2</sub> and 2.5-3% S or WO <sub>3</sub> + S.	Jern: <i>Zhur. Priklad. Khim.</i> , 7, 145-158 (1935).
Destructive hydrogenation of naphthalene and Tetralin to liquid products; T. 510-570°; initial pressure, 100-120 atm.; T. 600-610°; yield, 70%.	MoS <sub>2</sub> on Al <sub>2</sub> O <sub>3</sub> (weak splitting catalyst requiring high temp.).	Jern: <i>Khim. Tverdogo Topliva</i> , 6, 831-842 (1935).
Hydrogenation of naphthalene to Tetralin; c.p. 205-207°; once-through over the catalyst (one hour).	Ni-Al reduced at 200°; 20% of the total amount of catalyst used.	Bag, Egupow and Wolokitin: <i>Prom. Org. Khim.</i> , 2, 141-144 (1936).
Hydrogenation of naphthalene, using acetic acid or Dekalin or a mixture of both as a solvent (the improved microhydrogenation apparatus is described).	PtO (Adams); Pt black on Al <sub>2</sub> O <sub>3</sub> or BaSO <sub>4</sub> ; Pd black on BaSO <sub>4</sub> .	Jackson and Jones: <i>J. Chem. Soc.</i> , 1936, 895-899.
Hydrogenation of hydrocarbons, particularly naphthalene, which is the chief constituent of light oils; obtained as a by-product in cracking natural gas to olefins; reaction carried out in atmosphere of H <sub>2</sub> ; T. 95-200°; tetrahydronaphthalene is formed; to obtain best results, the ratio of the total pressure to the hydrogenation temp. is maintained at 1.388 pH <sub>2</sub> where pH <sub>2</sub> is the partial H <sub>2</sub> pressure.	Ni, Co, Pt, Pd; Ni-Co, Ni-Hg, Ni-Th, Ni-Mo, Ni-Cr; Ni on powdered pumice is especially active.	Smith and Rall: U.S.P. 2,101,104, Dec. 7, 1937.
Destructive hydrogenation of naphthalene and hydrogenated naphthalenes.	Mixtures of H <sub>2</sub> adding metals or metallic oxides with difficultly reducible metal oxides of the 2nd to 7th groups of the periodic system in which the metals are bound to H <sub>2</sub> PO <sub>4</sub> ; these metals and metal oxides may be used alone or mixed with their phosphates.	Deutsche Hydrierwerke A.-G.: G.P. 659,569. G.P. 659,673, Kl 12o, May 12, 1938.



Table 36 (Continued).

Reaction	Catalyst	Observer
Selective hydrogenation of naphthalene derivatives, using dioxane as a solvent; 0.25 mol 1-oxynaphthalene to 5,6,7,8-tetrahydronaphthol-(1); (1) T. 180°; time, 9 hrs.; (2) T. 155°; time, 6 hrs.; reaction with Ni at 100° is complete after 1-3 hrs.; reaction with Cu—Cr oxide at 200° is complete after 4 hrs.; hydrogenation of the second ring with Ni starts at 100°, while with Cu—Cr oxide it is still stable at 200°.	(1) 5 g. Cu—Cr oxide or (2) Raney's Ni.	Musser and Adkins: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 664-669 (1938).
Hydrogenation of naphthalene to tetrahydronaphthalene.	Metals K and Na precipitated on kieselguhr.	Compagnie de Produits Chimiques et Electrons (Alais, Froges et Camarque).
Destructive and normal hydrogenation of naphthalene to light products and also those with higher molecular weight with good properties as middle and lubricating oils (review in which characteristics of hydrogenation products, tables and diagrams are given).	Highly active.	Doldi: <i>Ann. chim. applicata</i> , <b>28</b> , 301-310 (1938).

Table 37. Catalytic Hydrogenation of Cresols and Naphthalene.

Reaction	Catalyst	Observer
Mutual hydrogenation of cresols and naphthalene; water formed in cresol hydrogenation poisons the catalyst.	(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> on active charcoal; Al <sub>2</sub> O <sub>3</sub> added in vapor phase splits the S cpds. (naphthalene impurities) and depoisons thereby the Mo catalyst poisoned by H <sub>2</sub> O.	Klukwin, Polozow and Lobusz: <i>Khim. Tverdogo Topliva</i> , <b>5</b> , 357-372 (1934).

Table 38. Catalytic Hydrogenation of Tetralin.

Reaction	Catalyst	Observer
Hydrogenation of Tetralin to Dekalin in the presence of three mols H <sub>2</sub> .	Ni.	Sabatier and Senderens: <i>Compt. rend.</i> , <b>132</b> , 1257 (1901). Leroux: <i>Ibid.</i> , <b>139</b> , 672 (1904).
Hydrogenation of Tetralin to Dekalin.	Pd.	Skita: <i>Ber.</i> , <b>45</b> , 3312 (1912).
Hydrogenation of Tetralin to Dekalin.	Pt.	Willstätter and associates: <i>Ber.</i> , <b>45</b> , 1471 (1912); <b>46</b> , 527 (1913); <b>57</b> , 638 (1924).
Hydrogenation of Tetralin to Dekalin in the presence of three mols H <sub>2</sub> .	Ni.	Wimmer: G.P. 300,052 (1915).
Hydrogenation of Tetralin to Dekalin.	Fe.	Tetralin G.m.b.H. (Schroeter): G.P. 324,861 (1915). G.P. 324,862 (1915).
Hydrogenation of Tetralin to Dekalin.	NiO + CuO, MnO, Pd, Pt. etc.	Agfa: G.P. 298,541 (1916). G.P. 301,275 (1917).

Table 39. Catalytic Hydrogenation of Anthracene.

Reaction	Catalyst	Observer
Hydrogenation of anthracene to decahydroanthracene.	Ni.	Lucas: <i>Ber.</i> , <b>21</b> , 2510 (1888).
Hydrogenation of anthracene to tetrahydroanthracene and octahydroanthracene at ordinary pressure; perhydroanthracene, C <sub>14</sub> H <sub>18</sub> , prepared from octahydroanthracene; (1) T. 250°; (2) at ordinary pressure.	(1) red P. (2) strongly reduced Ni.	Godchot: <i>Compt. rend.</i> , <b>139</b> , 605 (1904). Godchot: <i>Ber.</i> , <b>22</b> , 979 (1889).

Table 39 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of anthracene and phenanthrene to tetrahydroanthracene; pressure, 100 atm.	NiO; Ni <sub>2</sub> O <sub>3</sub> .	Ipatieff, Jakovlev and Rakitin: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>40</b> , 493 (1908). Ipatieff, Jakovlev and Rakitin: <i>Ber.</i> , <b>41</b> , 996 (1908).
Hydrogenation of anthracene to octahydroanthracene.	Ni.	Tetralin G.m.b.H. (Schroeter): G.P. 305,104 (1916). G.P. 352,719 (1920). G.P. 352,721 (1920).
Hydrogenation of $\alpha$ - and $\beta$ -oxy- and amino- derivatives of anthracene.	Ni salts.	Braun and Bayer: <i>Ann.</i> , <b>472</b> , 90-121 (1930).
Hydrogenation (very rapid) of anthracene; initial temp. 120°; yield, 50%; mesodihydroanthracene and small amounts of hexa- and octahydroanthracene obtained, together with tetrahydroanthracene.	NaH.	Hugel and Fries: <i>Ann. combustibles liquides</i> , <b>6</b> , 1109-1147 (1932).
Hydrogenation of an anthracene fraction from coal tar and crude anthracene to a yellow liquid; hydrogenation into aromatic hydrocarbons may be carried out in one step at 475° under 300 atm. H <sub>2</sub> pressure; duration of reaction, 2 hrs.; three cycles convert anthracene into 54% aromatic hydrocarbons; when coking gas containing H <sub>2</sub> is used instead of pure H <sub>2</sub> , five cycles instead of three cycles are required.	MoS <sub>3</sub> .	Straler and Moissejenko: <i>Khim Tverdogo Topliva</i> , <b>6</b> , 161-171 (1935).
Destructive hydrogenation of anthracene to pure low-boiling aromatic products; T. 480°; initial pressure, 100 atm. H <sub>2</sub> ; when temp. is decreased to 400° and pressure is increased to 120 atm. H <sub>2</sub> , hydrogenation leads to formation of mono- and bicyclic naphthenes, as well as saturated hydrocarbons; c.p. 270-275°; a mixture of perhydroanthracene and perhydrophenanthrene is obtained.	MoS <sub>3</sub> .	Prokopetz and Chadshinow: <i>Ibid.</i> , <b>6</b> , 347-353 (1935).
Hydrogenation of anthracene to octahydroanthracene (T. 180-220°, pressure about 100 atm.) to perhydroanthracene (C <sub>14</sub> H <sub>18</sub> ); T. 260-270° (anthracene from a pure commercial preparation is recrystallized from toluene, washed with 30% H <sub>2</sub> SO <sub>4</sub> , 2 N KOH and water, recrystallized again (216-216.8°); gaseous hydrocarbons not obtained by hydrogenation).	Ni—kieselguhr (10%).	Waterman, Leendertse and Crancoudouk: <i>Rec. trav. chim.</i> , <b>58</b> , 83-92 (1939).

Table 40. Catalytic Hydrogenation of Phenanthrene.

Reaction	Catalyst	Observer
Hydrogenation of phenanthrene to octanthrene.	Ni.	Tetralin G.m.b.H. (Schroeter): G.P. 352,721 (1920). Tetralin G.m.b.H. (Schroeter): <i>Ber.</i> , <b>37</b> , 1990 (1924).
Hydrogenation of sulfur-containing phenanthrene or gasoline.	A hydrogenation catalyst not sensitive to S; an aqueous solution of ammonium molybdate is mixed with an aqueous solution of chromium nitrate; a ppt. of chromium molybdate is obtained; H <sub>2</sub> S (H <sub>2</sub> Se, H <sub>2</sub> Te) is led through this mixture until apple green color is replaced by dark brown; an acid is added until the mother liquor becomes	Dupont (Lazier): U.S.P. 2,105,665, Jan. 18, 1938.

Table 40 (Continued).

Reaction	Catalyst	Observer
	colorless; the ppt. is filtered, washed and dried; Fe, Mn, Cu or Ni may be used instead of Cr; this catalyst is also suitable for hydrogenation of toluene to hexahydrotoluene; of naphthalene to Tetralin and Dekalin and a mixture of 75% hydrogen and 25% ethylene to ethane and pyridine to hexahydropyridine, etc.	

Table 41. Catalytic Hydrogenation of Terpenes.

Reaction	Catalyst	Observer
Hydrogenation of terpenes to polymethylene hydrocarbons or hydroaromatics.	Catalytically active Ni.	Sabatier and Senderens: <i>Compt. rend.</i> , 132, 1333 (1901).
Hydrogenation of limonene to hexahydrocymene.	Ni.	Ipatieff: <i>Ber.</i> , 43, 3546 (1910). Ipatieff: <i>J. Russ. Phys.-Chem. Soc.</i> , 42, 1563 (1910).
Hydrogenation of pinene to hydrocymene.		
Hydrogenation of terpenes (carvone, pulegone and menthone).	Ni <sub>2</sub> O <sub>3</sub> .	Ipatieff and Balatschinsky: <i>Ber.</i> , 44, 3461 (1911). Ipatieff and Balatschinsky: <i>J. Russ. Phys.-Chem. Soc.</i> , 43, 1754 (1911).
Hydrogenation of geraniol (alcohol) which may be oxidized to citral (aldehyde) at 140–180° under 1 to 4 atm. pressure.	Ni.	Armstrong and Hilditch: <i>Proc. Roy. Soc. London (A)</i> , 100, 240–252 (1921).
Selective hydrogenation of geraniol.		Grignard and Escourrou: <i>Bull. soc. chim.</i> , 37, 546–548 (1925).
Hydrogenation of citral, geraniol and limonene (dehydrocymol) under diminished pressure.	Pt oxide; Pt black with promoter.	Escourrou: <i>Ibid.</i> , 43, 1101–1115, 1204–1214 (1928).
Hydrogenation of terpenes.	Molybdic, vanadic, phosphoric and tungstic acids, the latter containing only 1–1.5% bound NH <sub>3</sub> ; also a tungstic acid prepared from sodium tungstate with 0.3% Na which is highly active.	Shering-Kahlbaum (Meerwein): G.P. 570,957, Kl 120, March 22, 1933.
Hydrogenation of limonene to <i>p</i> -cymene and <i>p</i> -menthane (menthane group). $3C_{10}H_{16} \rightarrow 2C_{10}H_{14} + C_{10}H_{20}$ <i>p</i> -cymene is separated from <i>p</i> -menthane by treatment with H <sub>2</sub> SO <sub>4</sub> , using the barium salt of <i>p</i> -cymene sulfonic acid.	Dehydrogenation catalysts; fuller's earth, kieselguhr, active charcoal, Al <sub>2</sub> O <sub>3</sub> .	Hercules Powder Co. (Humphrey): U.S.P. 1,893,802, Jan. 10, 1933.
Hydrogenation of cyclic terpene alcohols at 220° for many hours to myrcene and small amounts of dipentene; action of the catalyst upon citral and citronellal is a sudden reaction at 135° with the formation of <i>p</i> -cymene and small amounts of citral; citronellal under the same treatment reacted at 99°, giving isopulegone and diisopulegone, as well as terpene hydrocarbons.	Activated charcoal.	Kimura: <i>J. Chem. Soc. Japan</i> , 53, 497–503 (1932); 54, 14–21 (1933); <i>Chem. Abs.</i> , 27, 266.
Hydrogenation of limonene (0.02–0.05 g.) on a semi-micro scale.	Pd black	Zechmeister and Cholnoky: <i>Chem.-Zig.</i> , 60, 655–656 (1936).
Hydrogenation of carvone to carvomenthone (faster in alcohol than in ether and in dilute than in conc. solution).	Pt black.	Taipale, Gutner and Remis: <i>Zhur. Obshchei Khim.</i> , 7 (69), 1378–1389 (1937).

Table 41 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of pulegone to menthol (1.5 liters/min.); T. 245°.	330 g. Ni—Al.	Bag. Egupow and Wolokitin: <i>Prom. Org. Khim.</i> , 2, 141-144 (1936).
Hydrogenation of citral to citronellal under normal pressure; yield 60%.		
Hydrogenation of terpene ether; mono-, bicyclo-, or polymerized terpenes are etherified with aliphatic, aromatic, and hydroaromatic alcohols in the presence of inorganic or organic acids ( $H_2SO_4$ , $H_3PO_4$ , <i>p</i> -toluene sulfonic acid, etc.) at 30-200°; the double bonds are then hydrogenated at 50-200° at 100-1000 atm. per sq. in., e.g., 1000 g. ethylene glycol, 1700 g. $\alpha$ -pinene, and 25 g. benzene sulfonic acid are heated to 40-60°; 675 g. glycol terpene ether obtained (stable against $O_2$ and light).	Pt, Pd, Ni.	Hercules Powder Co. (Humphrey); U.S.P. 2,151,769, March 28, 1939.

Table 42. Catalytic Hydrogenation of Borneol.

Reaction	Catalyst	Observer
Hydrogenation of bornyl chloride.	Metal Na (in a boiling benzene solution).	Köhler and Schnitzer: <i>Ber.</i> , 13, 2236 (1880).
Hydrogenation of borneol to camphene.	$Al_2O_3$ and CuO.	Kiszner: <i>J. Russ. Phys.-Chem. Soc.</i> , 43, 592 (1911). Kiszner: <i>Ber.</i> , 40, 2750 (1907).
Hydrogenation of borneol to camphor.	Hexapropionate.	Müller: G.P. 307,380, Kl 12g Gr 2, March 26, 1916.
Hydrogenation of borneol to camphor.	Reduced Cu.	Mesumoto: <i>Mem. Coll. Eng., Kyoto Imp. Univ.</i> , 9, 219-224 (1925).
Hydrogenation of camphor; T. 460°.	$PtO + PtO_2$ (the ordinary Pt black, if previously used for the hydrogenation of phenol or o-allyl phenol, does not hydrogenate camphor).	Laffitte and Grandadam: <i>Congr. chim. ind., 15th Congr., Brussels</i> , 1, 319-323 (1935).

Table 43. Catalytic Hydrogenation of Pinene and Nopinene.

Reaction	Catalyst	Observer
Hydrogenation of pinene or nopinene to camphene; conversion of nopinene to pinene.	Normal salts of $H_2SO_4$ which retain one mol water of crystallization at 120-220°, e.g., $MgSO_4 \cdot 7H_2O$ , $NiSO_4 \cdot 7H_2O$ .	Shering-Kahlbaum A.-G.; F.P. 747,349, June 4, 1933.
Hydrogenation of pinene chlorhydrate to camphor; pinene chlorhydrate is heated in a mixture with naphthenates to which excess alkali has been added.	Cu.	Salkind and Gertschikow: <i>Russ. P.</i> 28,907, Jan. 31, 1933.
Hydrogenation of pinene or nopinene to camphene; catalyst poured into Cu tubes and heated to 325° over which a mixture of one part pinene and 4 parts water is passed rapidly.	10 parts $H_2PO_3$ and 6 parts $H_3BO_3$ are dehydrated at 250° and heated dry; powdered boric acid and phosphoric acid are placed on pumice.	Shering-Kahlbaum A.-G. (Schwenk and Schmidt); G.P. 578,569, Kl 12o, June 15, 1933.
Hydrogenation of pinene (5 g.); T. 100°; conversion of terpenes by dehydration.	Acids such as antimonie, stannic, titanie, tungstic, phosphoric-tungstic, as well as their acid salts.	Shering-Kahlbaum A.-G. (Meerwein); G.P. 584,965, Kl 12o, Sept. 29, 1933.
Hydrogenation of pinene or nopinene to camphene in the presence of oxalic acid.	Silica gel.	Kuwata and Tategar: <i>J. Soc. Chem. Ind. Japan</i> , 35, 303B-304B (1932).

Table 43 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of pinene or nopinene to camphene; conversion of nopinene into pinene (both continuity and high efficiency attained by converting them into salts by means of bases).	Inorganic acids such as titanitic, silicic, vanadic, arsenic, molybdic, antimonic, tungstic; complex acids such as boric-tungstic, tungstic-silicic, stannic-phosphoric, boric-acetic, aluminum-oxalic; acid salts and phosphates of Mg, Mn, or U.	Shering-Kahlbaum A.-G.: F.P. 739,770, July 7, 1932.
Hydrogenation of unsaturated cyclic hydro-carbons (olefinic terpenes and $\alpha$ -pinene); irreversible reaction.		Zelinsky: <i>Ber.</i> , <b>58</b> , 864-869 (1925)
Hydrogenation of pinene or nopinene to camphene; conversion of nopinene into pinene.		Shering-Kahlbaum A.-G.: E.P. 391,073, May 11, 1933.

Table 44. Catalytic Hydrogenation of Fats.

Reaction	Catalyst	Observer
Hydrogenation of fats in liquid phase at high temp.; addition of H <sub>2</sub> to high molecular weight fatty acids and liquid fats.	Ni.	Herforder Maschinenfett-Ölwerke Leprince und Siveke (Normann): G.P. 141,029 (1902).
Hydrogenation of fats.	Ni.	Erdmann: G.P. 211,669 (1907). Bedford: G.P. 221,890 (1907).
Hydrogenation of fats; oil is thrown and hydrogenated simultaneously.	Pd on carrier; Co, Cu, Fe, inactive.	Verein Chemische Werke (Paal): G.P. 236,488 (1910). Schlink & Co. A.-G. (Paal): G.P. 252,320, Kl 53H Gr 1, Jan. 31, 1911. E.P. 5,188 (1911).
Hydrogenation of fats.	Ni on kieselguhr.	Kayser: U.S.P. 1,004,035 (1911). U.S.P. 1,008,474 (1911).
Hydrogenation of fats.	Ni on charcoal.	Ellis: U.S.P. 1,060,673 (1912).
Hydrogenation of fats.	NiO.	Ipatieff: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>45</b> , 1464 (1913).
Hydrogenation of fats.	Metal Ni.	Ipatieff: <i>Ibid.</i> , <b>46</b> , 302 (1914).
Hydrogenation of fats.	Ni on charcoal.	Dewar: B.P. 15,668 (1914).
Hydrogenation of fats.	Os oxide.	Lehmann: <i>Arch. pharm.</i> , <b>251</b> , 152-153. Normann and Schick: <i>Ann.</i> , <b>257</b> , 152 (1914).
Hydrogenation of fats.	Ni with other oxides.	Badische Anilin- und Soda Fabrik: G.P. 282,782 (1915).
Hydrogenation of fats at room temperature.	Ni on charcoal or bleaching earth; Ni precipitated on pure silicic acid is less active than Ni precipitated on silicic acid containing Al <sub>2</sub> O <sub>3</sub> .	Kelber: <i>Ber.</i> , <b>49</b> , 55 (1916).
Hydrogenation of fats.	Ni benzoate mixed with kieselguhr.	Bremen-Besigheimer Ölfabriken: G.P. 299,741 (1917).
Hydrogenation of fats.	Ni with Al <sub>2</sub> O <sub>3</sub> .	Badische Anilin- und Soda Fabrik: G.P. 307,580 (1918).
Hydrogenation of fats.	Ni on kieselguhr.	Krezil: "Kieselguhr Verwendung," p. 113, (1936). Ubbelohde and Svanoe: <i>Z. angew. Chem.</i> , <b>32</b> , 257, 269 (1919).
Hydrogenation of fats; mixing of oil after reduction in a CO <sub>2</sub> atmosphere.	Stable contact mass.	Bremen-Besigheimer Ölfabriken: G.P. 286,789, Kl 23d, Dec. 18, 1910 G.P. 312,427, Kl 23d Gr 1, May 30, 1912.
Hydrogenation of fats.	Ni.	Bremen-Besigheimer Ölfabriken: G.P. 314,685, Kl 12g Gr 2, Jan. 2, 1916.

Table 44 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of fats.	Ni as a fatty acid salt.	De Nordiske Fabriken de Kadt: G.P. 365,979 (1919).
Hydrogenation of fats.	Pd.	Nord: <i>Z. angew. Chem.</i> , <b>32</b> , 1380, Dec. 16, 1919.
Hydrogenation of unsaturated fats.	Ni.	Armstrong and Hilditch: <i>Proc. Roy. Soc. London (A)</i> , <b>96</b> , 137-146 (1919).
Hydrogenation of fats.	Kieselguhr impregnated with Ni tetracarbonyl and heated until metallic Ni is formed; reduced to a paste with oil.	Schicht A.-G.: Aust. P. 70,775 (1919).
Hydrogenation of fats at 40-100°.	Ni formate or Ni acetate precipitated on kieselguhr and heated in an inert gas; catalyst decomposed at 270-280°.	Brochet: E.P. 139,510 (1919). Sinowjew: <i>Vsesoyuz. Tseniral. Nauch.-Issledonatel. Inst. Zhiron (Trudy VNIIZh)</i> , <b>3</b> , 134. Rees: U.S.P. 1,511,520 (1925).
Hydrogenation of fats.	Ni in compact form.	Hagemann and Baskerville: U.S.P. 1,083,930 (1914). Bolton: E.P. 162,376 (1920). Technical Research Works, Ltd. (London) (Lush): E.P. 203,218 (1922).
Hydrogenation of fats.	NiCO <sub>3</sub> or Ni formate mixed with gelatinous silicic acid (salts decomposed at 235-250°); a mixture of NiO and Ni(OH) <sub>2</sub> , the hydrate containing silicic acid, reduced by heat in the presence of H <sub>2</sub> .	Spieter: U.S.P. 1,139,592 (1920). Schicht and Mielck: Austrian P. 88,453, May 10, 1922.
Hydrogenation of fats.	Pulverized metals or their sub-oxides.	Ellis: E.P. 162,038, May 19, 1921.
Hydrogenation of fats and oils; a continuous process.	Ni on wool.	Bolton: E.P. 162,370, May 23, 1921.
Hydrogenation of fats and oils; a suggestion is made for maintaining the activity of the catalyst.	Metals.	Bolton and Lush: E.P. 162,382, May 26, 1921.
Hydrogenation of fats.	Metals; a method for regenerating the catalyst is used.	Goslings: Austrian P. 88,193, April 25, 1922. U.S.P. 1,419,986, June 20, 1922.
Hydrogenation of fats at 180°.	Ni (time of action short).	Schicht and Mielck: Aust. P. 88,453, May 10, 1922.
Hydrogenation of fats.	Ni on kieselguhr; the addition of 1-2% Al <sub>2</sub> O <sub>3</sub> promoted the reaction; if kieselguhr is extracted with acid before precipitating the nickel, the activity of Ni on kieselguhr is decreased.	Armstrong and Hilditch: <i>Proc. Roy. Soc. London (A)</i> , <b>103</b> , 586 (1923); refer to the statement of Grün and Mielck in W. Fahrion's "Die Härtung der Fette," 2nd Ed., p. 103, (1921). Erdmann: <i>J. prakt. Chem.</i> , <b>87</b> , 425 (1913).
Hydrogenation of fats and oils.	Ni.	Granichstädter and Sittig: Dutch P. 6,568, May 15, 1922. Rita and Mazune: <i>Z. angew. Chem.</i> , <b>36</b> , 389-391 (1923).
Hydrogenation of fats.		Ritter: <i>J. Phys. Chem.</i> , <b>25</b> , 89 (1921); <b>28</b> , 59 (1924). refer also to a review by Margoshes: <i>Seifensieder-Ztg.</i> , <b>43</b> , 951.
Hydrogenation of fats.	Ni formate.	Foster Co.: U.S.P. 1,519,088, Dec. 9, 1924.
Hydrogenation of fats.	Cu, Ni, Fe, Co, Pt melted together on chamotte.	Harter and Meyer: G.P. 401,010, Kl 23d, Aug. 25, 1924.

Table 44 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of fats.	Fe <sub>2</sub> O <sub>3</sub> .	Gyro Process Corporation (Komagage): U.S.P. 1,687,890 (1925). Gyro Process Corporation (Weaver): U.S.P. 1,708,247 (1925).
Hydrogenation of fats.	Ni + Na <sub>2</sub> CO <sub>3</sub> (water vapor slows down the reaction).	Rita, Mazume and Rino: <i>Mem. Coll. Sci., Kyoto Imp. Univ.</i> , 3 (N7).
Hydrogenation of fats.	Ni formate, Na <sub>2</sub> BO <sub>3</sub> .	Rita, Mazume and Rino: <i>Chem. Umschau. Fette, Öle, Wachse, Harze</i> , 32, 262-265 (1925).
Hydrogenation of fats.	Electrolytic Ni.	Swizyn: <i>Masloboino Zhirovoe Delo</i> , 3, 25 (1928).
Hydrogenation of fats.	Ni borate.	Ubbelohde and Schönfeld: <i>Allgem. Oel Fett-Ztg.</i> , 27, 425-426 (1930). refer also to Princess: <i>Seifensieder-Ztg.</i> , 56, 298 (1928).
Hydrogenation of fats.	Ni on kieselguhr (action promoted by oxides of rare earths); Cu.	Ssadikow: <i>Zhur. Priklad. Khim.</i> , 3, 573 (1930). Moschkin and Artemow: <i>Masloboino Zhirovoe Delo</i> , 4/5, 27 (1932). Badische Anilin- und Soda Fabrik: G.P. 307,580 (1920).
Hydrogenation of fats.		Armstrong: <i>J. Soc. Chem. Ind.</i> , 50, 968-970. Armstrong: <i>Chem. Trade J.</i> , 89, 448-450 (1931).
Hydrogenation of fats.	Ni on carrier (activity increases in sequence); bone charcoal, Al <sub>2</sub> O <sub>3</sub> and kieselguhr.	Kailan and Stüber: <i>Monatsh.</i> , 62, 90 (1933).
Hydrogenation of fats.	Pd; non-conducting catalysts precipitated on a conducting material or mixed with it; catalysts agitated by means of a high voltage (direct or alternate current); voltage held below that required for a spark discharge.	Mentzel: E.P. 385,273, Jan. 19, 1933.
Hydrogenation of fats and oils.	Ni.	Seehof: <i>Metallbörse</i> , 24, 453-454 (1934).
Hydrogenation of fats.	Ni on kieselguhr; activity reverses and is proportional to the content of silicic acid in the kieselguhr; activity of the catalyst increases with the solubility of the kieselguhr in sulfuric acid.	Botkowskaja and Artamonow: <i>Masloboino Zhirovoe Delo</i> , 468 (1935).
Hydrogenation of fats.	Ni borate on kieselguhr; Ni salt solution precipitated on kieselguhr with NaCO <sub>3</sub> and sodium tetraborate; 15% boric acid anhydride decreases considerably the inflammability.	Belani: <i>Allgem. Oel Fett-Ztg.</i> , 23, 420 (1936).
Hydrogenation of fats.	Ni—Cu catalyst (obtained from pyridine complex salts of formates) precipitated on kieselguhr; the catalyst-carrier is prepared by dissolving the formates in pyridine, using heat, sucking off pyridine under a slight heating in vacuum and evaporating to dryness under stirring; the catalyst is reduced in a H <sub>2</sub> stream at 220° and cooled in CO <sub>2</sub> stream (reduction of the catalyst at 220° yields more active catalyst than if reduced at 280°; at lower temp. the action was not much less); Ni is activated by Cu; the best mixing ratio for aqueous formate solution 1 : 1 in case of Cu—Ni; pyridine complex was 70% Cu and 30% Ni; Ni—Cu—Co gave no better results; using pyridine as solvent instead of water for Ni and Cu formate gives much more active catalysts.	Kaufmann: <i>Fette u. Seifen</i> , 45, 304-306 (1938).

Table 44 (Continued).

Reaction	Catalyst	Observer
Catalytic hydrogenation of fats; by hydrogenating in an autoclave and by destructive hydrogenation; likewise addition of Cu to the catalyst is advantageous, e.g., 25 g. soybean oil; catalyst preheated at 220° passed through CO for 1½ hr. and then subjected to the action of H <sub>2</sub> (electrolytic); 25 l. per hr.; duration 3 hrs.	Ni catalyst (0.1%) + Cu (Cu has no influence) (prepared from Ni and Cu formate solution and ground fine); but when using mixed metal catalysts: carrier substance (1 : 9) with amount of Ni remaining constant (0.1%) Cu acted as an activator; addition of 10% Cu accelerates H <sub>2</sub> adsorption in the first part of the hydrogenation process, while toward the end contrary to the use of pure Ni, a slowing down takes place; on addition of 100% Cu with respect to Ni the maximum is achieved; addition of larger amounts of Cu shows a small increase in the activity; 0.04% Ni in the presence of 0.05% Cu may substitute the four-fold amount of Ni; it is believed that small addition of Cu loosens the Ni lattice by incorporating Cu atoms; larger additions of Cu cause formation of colloidal Cu originating from the excess formate which spreads as a cloud around the active places of the Ni catalyst and so makes difficult the diffusion of H <sub>2</sub> toward them.	Kaufman and Pardun: <i>Fette u. Seifen</i> , <b>45</b> , 223-228 (1938).
High-pressure hydrogenation of mixtures of fats, especially those which decompose readily; also mineral oils; T. 200-400°; pressure 50-200 atm.; mixtures of hydrocarbons are obtained; low-boiling hydrocarbons, used as motor fuels, and high-boiling hydrocarbons as lubricating oils, especially cutting and textile oils; the fats are completely reduced to hydrocarbons.	Nickel.	Deutsche Hydrierwerke A.-G.: U.S.P. 2,163,563, June 20, 1939

Table 45. Catalytic Hydrogenation of Oils.

Reaction	Catalyst	Observer
Hydrogenation of oils.	1 part by weight Pd in 10,000 parts by weight oil.	Day: U.S.P. 826,089, July 17, 1906.
Hydrogenation of oils.	Ni stearate; decomposed in a fatty oil in vacuum; a stream of CO <sub>2</sub> or N <sub>2</sub> serves to prepare a carbon-containing Ni catalyst.	Higgins: E.P. 2,104 (1913).
Hydrogenation of oils.	Ni oxalate and an aqueous solution of Al nitrate evaporated to dryness and reduced at 300-350° in the presence of H <sub>2</sub> .	Badische Anilin- und Soda Fabrik: G.P. 307,580 (1919).
Hydrogenation of oils.	Ni salt with Na aluminate precipitated in the presence of kieselguhr.	De Nordiske Fabriken de Kadt: Dutch P. 7,970 (1924); (Refer to C. 1925 I 588). E.P. 140,371 (1919).
Hydrogenation of oils.	Ni carbonate or Ni formate mixed with Al <sub>2</sub> O <sub>3</sub> in a gelatinous form, dried and decomposed under oil.	Spieter: U.S.P. 1,139,592 (1920).
Hydrogenation of oils.	Ni—fuller's earth.	Larkin Co.: U.S.P. 1,232,830 (1918).
Hydrogenation of oils.	Ni carbonyl.	Lessing: E.P. 152,740, Nov. 18, 1920. Lessing: <i>J. Soc. Chem. Ind.</i> , <b>40</b> , 445-447 (1921).
Hydrogenation of oils.	Ni.	Armstrong and Hilditch: <i>Proc. Roy. Soc. London (A)</i> , <b>99</b> , 490-495, Sept. 1, 1920.
Hydrogenation of oils in a liquid phase.	Active metals.	Brochet: <i>Bull. soc. chim.</i> <b>27</b> , 897 (1920).
Hydrogenation of oils.	Kieselguhr impregnated with a Ni salt solution; after drying, impregnated with paraffin; Ni-charcoal-kieselguhr catalyst.	Ellis: E.P. 162,038 (1921). E.P. 523,334 (1921).
Hydrogenation of oils.	Aqueous Ni nitrate solution and cane sugar solution evaporated, heated to dryness and precipitated at 550-650° in a stream of CO <sub>2</sub> .	Schuck: E.P. 122,192, April 6, 1920. E.P. 142,576 (1921). Erdmann and Bedford: G.P. 260,009 (1912).



Table 45 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of oils.	Ni or Ni cpds. impregnated with readily carbonized organic substances, such as cane sugar or oil, and treated at ordinary temp. with $\text{H}_2\text{SO}_4$ ; the catalyst contains finely divided colloidal carbon.	Arldt: G.P. 356,614 (1921).
Hydrogenation of oils.	Ni suboxide hydrate and charcoal reduced in a stream of $\text{H}_2$ at $300^\circ$ in the absence of air and mixed at once with the oil; more active than pure Ni.	Ellis: U.S.P. 1,088,673, Feb. 24, 1914. U.S.P. 1,095,144 (1915).
Hydrogenation of oils.	Ni precipitated on charcoal and reduced at $350^\circ$ .	Kahlenberg and Ritter: (1915-1916).
Hydrogenation of oils.	Ni on a mixture of charcoal and kieselguhr, "silica black."	Williams and Jacobson: <i>Ind. Eng. Chem.</i> , <b>26</b> , 800 (1934).
Hydrogenation of oils.	Gas-activated charcoal as carrier.	N. V. Allgemeine Norit Mij: Dutch P. 12,851.
Hydrogenation of oils at 150-160°; oils bleached and decolorized.	Ni + Mg or Al salts.	Granichstädter and Sittig: Aust. P. 85,954, Oct. 25, 1921. E.P. 147,578, Nov. 10, 1921.
Hydrogenation of oils.	Sn.	Riebeckische Montanwerke A.-G.: G.P. 559,898, May 27, 1922.
Hydrogenation of oils.	Mixed catalysts.	Patel: <i>J. Indian Inst. Sci.</i> , <b>7</b> , 197-204 (1924).
Hydrogenation of oils.	Ni-silicate; Ni-tungstate.	Kahlenberg and Pi: <i>J. Phys. Chem.</i> , <b>28</b> , 39-70 (1924).
Hydrogenation and bleaching of oils.	Ni.	Granichstädter and Sittig: G.P. 402,784, Cl 12g, Gr 2, Sept. 19, 1924. Société Anonym Oxydrique (Malakoff): G.P. 409,714, Cl 12o, Gr 27, Feb. 14, 1925.
Hydrogenation of oils.	Melted Sn.	Trautmann: E.P. 261,987, Jan. 19, 1927.
Hydrogenation of oils.	$\text{AlCl}_3$ , $\text{SnCl}_4$ , $\text{FeCl}_3$ and $\text{BF}_3$ .	I. G. Farbenindustrie A.-G.: F.P. 655,376, April 18, 1929.
Hydrogenation of hydrocarbon oils in vapor phase.	$\text{Fe}_2\text{O}_3$ containing small amounts of Sn or metals of the 5th or 6th group, such as Mo, V, W, Cr; $\text{O}_2$ is blown into the melted Fe to which $(\text{NH}_4)_2\text{MoO}_4$ or $\text{Cr}_2\text{O}_3$ is added.	Imperial Chemical Industries, Ltd. (Harper and Scott): F.P. 361,135, Dec. 10, 1931. E.P. 359,108, Nov. 12, 1931. E.P. 359,755, 1931.
Hydrogenation of oils.	Pt and Pd on kieselguhr as active as Ni on kieselguhr.	Kailan and Kohberger: <i>Monatsh.</i> , <b>59</b> , 16 (1932).
Hydrogenation of oils.	$\text{Ni}_2\text{Cr}_2\text{O}_5$ (prepared from Ni chromate by heating and reduction).	Catalyst Research Corporation (Bennett): U.S.P. 1,893,155, Jan. 3, 1932.
Hydrogenation of hydrocarbon oils in vapor phase; T. 850-1050°F. pressure, 200 atm.	Sulfides of Cr, Mo and W.	Standard I. G. Co. (Harding): E.P. 386,299, Feb. 9, 1933.
Hydrogenation of the kerosene fraction of Rumanian crude oil of Moreni.	$\text{MoS}_2 + \text{MoO}_3 + \text{Al}_2\text{O}_3$ .	Căndeia and Marshall: <i>Congr. chim. ind.</i> , 15th Congr., <i>Brussels</i> , <b>1</b> , 542-560 (1935).
Hydrogenation of neutral oils from low-temp. tars by treatment with $\text{NaOH}$ ; T. $470^\circ$ ; pressure, 100 atm. $\text{H}_2$ ; yield, with $\text{MoO}_3$ , 80.3% with $\text{MoS}_2$ , 69.0% and 48.3% with $\text{SnCl}_4$ , 72.5% and 44.6%	$\text{MoO}_3$ , $\text{MoS}_2$ , $(\text{NH}_4)_2\text{MoO}_4$ , $\text{SnCl}_4$ , $\text{Fe}_2\text{O}_3$ , $\text{NiO}$ , $\text{ZnCl}_2$ , $\text{FeCl}_3$ , $\text{CoS}$ , $\text{ZnO}$ , $\text{Cr}_2\text{O}_3$ .	Ando: <i>J. Soc. Chem. Ind. Japan</i> , <b>38</b> , 267B-269B (1935).

Table 45 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of hydrocarbon oils.	Mixture of equimolecular amounts of $\text{AlCl}_3$ and phenol (mild action).	Gulf Refining Co. (Stevens): U.S.P. 1,999,345, April 30, 1935. U.S.P. 2,001,634, May 14, 1935.
Hydrogenation of oils, lignite, pitch and other C-containing substances; pretreated by heating to 280–400°; $\text{CO}_2$ and $\text{H}_2\text{S}$ , usually formed, removed; pretreatment may follow subjection to pressure up to 200 atm.; a temp. increase, due to reaction between $\text{O}_2$ and $\text{H}_2$ to form $\text{CH}_4$ , to be avoided; substances to be hydrogenated reduced to paste with oil and mixed with catalyst.		International Hydrogenation Patents Co.: F.P. 792,591, Jan. 6, 1936.
Hydrogenation of crude oil; the reaction mixture is subjected to a high voltage (alternating current), and electric stirring increases the reaction velocity.	0.024% Ni.	Sato and Seto (Japan): Danish P. 52,057, Aug. 24, 1936.
Hydrogenation of oils.	Salts of Ni: formate, acetate, propionate, butyrate, oxalate, oleate or citrate; 510 g. $\text{Ni}(\text{OOCH})_2 \cdot 2\text{H}_2\text{O}$ are dispersed in powder form in 1500 cc. of a mixture containing di-, tri-, tetraisobutylene; di-, triisomylene, or isooctane, dodecane and water heated in an autoclave to 300°; gaseous reaction products are removed from time to time $\text{Ni}(\text{OOCH})_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ni} + 2\text{CO}_2 + 2\text{H}_2\text{O} + \text{H}_2$	Shell Development Co. (Williams and McAllister): U.S.P. 2,067,368, Jan. 12, 1937.
Hydrogenation of S-rich petroleum; light petroleum fractions up to 300° are desulfurized at 400–420° under 20 atm. pressure; residue boiling above 300°, and the oil fractions obtained therefrom are desulfurized at 400° under 150–200 atm. pressure to prepare oils with less than 0.2% S, or subjected to a destructive hydrogenation at 420–450° under 150–200 atm. pressure to obtain S-free benzene and kerosene; the medium oil fractions are subjected to hydrogenation in vapor phase at 500–540° under 150–200 atm. pressure to obtain benzene with better antiknock properties.	$\text{MoS}_2$ and $\text{Cr}_2\text{O}_3$ .	Putschkow: <i>Nefyanos Khos.</i> , 6, 44–51 (1937).
Hydrogenation of a hydrocarbon oil consisting of abietane ( $\text{C}_{19}\text{H}_{36}$ ) and abietine ( $\text{C}_{19}\text{H}_{34}$ ) in liquid phase; T. at least 140°; pressure, 21 atm.; four $\text{H}_2$ atoms required for each mol. of abietane, as well as abietine; hydrogenation carried out to obtain either octahydroretene or hexyhydroabietine; oils decolorized and rendered stable against light and air.	Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and/or Pt precipitated on kieselguhr or asbestos; neutral oils may be hydrogenated over Na.	Hasselstrom and Hull: U.S.P. 2,095,548, Oct. 12, 1937.
Hydrogenation of liquid or melted hydrocarbons, water-poor oils containing phenols or N cpds.; two steps in process: (1) refining: T. 410°; pressure, 250 atm. (2) cracking: T. 380°; pressure, 200 atm. the mixture of benzene obtained from both steps of hydrogenation has an octane number of 65.5.	10% tungsten sulfide. 90% terrane earth.	International Hydrogenation Patents Co., Ltd.: F.P. 826,236, March 25, 1938.
Destructive hydrogenation of petroleum residues from Bucsan; the saturation of unsaturated cracking products is satisfactory only at 430° and in the presence of catalysts and by using sufficiently high $\text{H}_2$ pres-	$\text{MoO}_3$ and $\text{MoS}_3$ ; $\text{MoO}_3$ causes strong hydrogenation with low yield in saturated benzenes, while $\text{MoS}_3$ on the contrary increases the benzene yield by a better cracking action.	Căndea and Saucine: <i>Petroleum</i> , 35, 361–63 (1939).

Table 46. Catalytic Hydrogenation of Fatty Oils.

Reaction	Catalyst	Observer
Hydrogenation of unsaturated fatty oils at 100–120°.	Ni(NO <sub>3</sub> ) <sub>2</sub> + Cr(NO <sub>3</sub> ) <sub>3</sub> precipitated with Na <sub>2</sub> CO <sub>3</sub> .	Badische Anilin- und Soda Fabrik: G.P. 362,143, Kl 12o, Oct. 23, 1921; add to G.P. 307,580 Rideal: <i>Mon. sci.</i> (5), 12, 3–9, 73–83 (1922).
Hydrogenation of fatty oils.	Active surface of Ni.	Jozsa: <i>Z. angew. Chem.</i> , 41, 767–771 (1927).
Hydrogenation of fatty oils, fats and waxes.	Dispersed Ni + Al (Al dissolved out from an alloy).	Raney: U.S.P. 1,628,190, May 10, 1927.
Hydrogenation of unsaturated fatty oils.	Active metal plus an organic acid, such as oxalic, benzoic, or phthalic, as well as fatty acids.	Naumlouze Vennootschap Industrie Maatschappi (van Noury and van der Lande): F.P. 550,143, Feb. 27, 1923.
Hydrogenation of fatty oils.	Ni on kieselguhr.	Uno and Saido: <i>J. Soc. Chem. Ind. Japan</i> , 30, 107B (1927).
Hydrogenation of unsaturated fatty oils.	Ni.	Masloboino <i>Zhirovoe Delo</i> , 46, 32–34 (1929).
Hydrogenation of fatty oils under pressure.	Japanese acid earth with a layer of Ni.	Tanaka and Kobayashi: <i>J. Soc. Chem. Ind. Japan</i> (Supplement), 35, 29B (1932).
Hydrogenation of fatty oils, using alcohol as a hydrogen generator.	Ni.	Ljubarski: <i>Zhur. Priklad. Khim.</i> , 5, 1025–1045 (1932).
Hydrogenation of unsaturated fatty oils at 200–400°.	Double chromate of a N cpd., such as NH <sub>3</sub> , aniline, methylamine, or pyridine, and a metal which hydrogenates, such as Fe, Ni, Co, Cu, Sn.	Dupont (Lazier): U.S.P. 1,964,000, June 26, 1934.

Table 47. Catalytic Hydrogenation of Mineral Oils.

Reaction	Catalyst	Observer
Hydrogenation of mineral oils.	Metals.	Steger and Bohnenblut: Schweiz. Ver. Elektrochem., <i>Monats-Bull.</i> , H3 (1924).
Hydrogenation of mineral oils.	Ammonium <i>p</i> -tungstate heated with H <sub>2</sub> S to 410° for 24–36 hrs. under 5 atm. pressure in absence of air; WS <sub>2</sub> formed under 200 atm. pressure, pressed into pieces and heated in a stream of H <sub>2</sub> up to 430°.	I. G. Farbenindustrie A.-G.: E.P. 251,264, July 7, 1926. E.P. 675,493, Feb. 11, 1930. E.P. 379,335, Sept. 22, 1932. F.P. 728,913, July 13, 1932.
Hydrogenation of mineral oils under pressure in the presence of 1–15% H <sub>2</sub> S in the hydrogenating gas so that the catalyst (metal oxides) may be converted into sulfides; instead of H <sub>2</sub> S, CS <sub>2</sub> or elemental S may be added.	Oxides of Fe, Co, Ni or other cpds.	Deutsche Gold und Silber Scheideanstalt (Roessler): F.P. 714,557, Nov. 17, 1931. Burstin and Winkler: <i>Crude Oil and Tar</i> (U.S.S.R.), 8, 425–430, 445–446 and 461–463, Oct. 15, 1932.
Hydrogenation of mineral oils or cracking of paraffinic waxes.	MoS <sub>3</sub> , WS <sub>3</sub> , CoS, NiS.	Tropsch: <i>Proc. Intern. Conf. Bituminous Coal</i> , 3rd Conf., 2, 35–48 (1931).
Hydrogenation of mineral oils under high pressure.	Ni ammonium oxide or hydroxide impregnated on white acid clay.	Tanaka, Misoshita, Maeda and Heno: Jap. P. 100,179, March 20, 1933.
Hydrogenation of mineral oils; the equilibrium constants calculated according to Nernst's formula show that unsaturated aliphatic hydrocarbons are hydrogenated at 477°, while above 300°, hydroaromatics are dehydrogenated; with the use of a catalyst containing Mo, olefins are hydrogenated, while aromatics remain almost unchanged and higher-boiling saturated hydrocarbons are split.	Catalyst containing Mo.	Fussteig: <i>Oesterr. Chem.-Zig.</i> , 38, 170–174 (1935).

Table 47 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of mineral oils distilled at 140–160°; T. 550°; pressure, 200 atm. H <sub>2</sub> .	Cpds. of I with As, Cu, Ti, Sn, Mn, Ni, or Co, or a mixture of the same, as well as of sulfides of metals of the 5th and 6th groups of the Periodic System.	International Hydrogenation Patents Co., Ltd.: Polish P. 24,181, Jan. 28, 1937.
Hydrogenation of asphalt-containing mineral oils and tars; T. 250°; partial H <sub>2</sub> pressure: atm. – 2% asphalt, 300–350 2–10% " , 350–420 10–20% " , 420–500 20–30% " , 500–600 Ash content of oils should be kept below 0.01% to prevent poisoning of the catalyst.	Sulfides or oxides of W, Mo, V, Rh.	International Hydrogenation Patents Co., Ltd.: E.P. 477,944, Feb. 3, 1938. F.P. 822,306, Dec. 28, 1937.
Hydrogenation of mineral oils; T. 400°; pressure, 200 atm.; yield, 60%.	70 parts by weight of a catalyst obtained from ammonium tungstate and H <sub>2</sub> S at 410° under 5 atm. pressure and 30 parts by weight MoBr <sub>3</sub> .	International Hydrogenation Patents Co., Ltd.: Polish P. 24,179, Jan. 25, 1937.
Hydrogenation of coal, tar and mineral oils under pressure.	The hot parts in the equipment consist of alloys containing more than 40% Ni, e.g., 13.8% Cr, 60.1% Ni, 24.2% Fe and 0.2% C, or 25.0% Fe, 17.0% Cr, 58.0% Ni and 0.03% C.	I. G. Farbenindustrie A.-G. (Krauch and Pier): G.P. 655,324, Kl 12o, Jan. 13, 1938.

Table 48. Catalytic Hydrogenation of Cottonseed Oil.

Reaction	Catalyst	Observer
Hydrogenation of cottonseed and linseed oils.	Ni, Co, Fe, Cu, NiCO <sub>3</sub> , Ni(NO <sub>3</sub> ) <sub>3</sub> .	Naamlose Vennootschap (Jurques); G.P. 282,782, Kl 12o Gr March 16, 1915.
Hydrogenation of cottonseed oil.		G.P. 272,340, Kl 12o Gr 27, March 26, 1912. G.P. 207,989, Kl 12o Gr 31, Nov. 22, 1907.
Hydrogenation of cottonseed oil.	Pt.	Richardson and Snoddy: <i>Ind. Eng. Chem.</i> , 18, 570–571 (1926).
Hydrogenation of cottonseed oil.	A contact mass containing a permuto-genetic body and a catalyst, but not a base-exchanging cpd.	Selden Co. (Jaeger): E.P. 306,803, April 24, 1929. Can. P. 296,913, Jan. 21, 1930.

Table 49. Catalytic Hydrogenation of Various Oils.

Reaction	Catalyst	Observer
Hydrogenation of fish oil.	Ni, Fe, Co.	Badische Anilin- u. Soda Fabrik: G.P. 307,580, Kl 12o Gr 27, June 22, 1913.
Hydrogenation of nut oil.	Ti, U, Mn, V, Ni, Ta.	G.P. 207,989, Kl 12o Gr, Nov. 22, 1907.
Hydrogenation of vegetable and train oils.		Bellwood: <i>Chem. Trade J.</i> , 76, 1925.
Hydrogenation of olive oil.	Colloidal Pt+0.1% saponin (shortens the time of hydrogenation).	Briesalski: <i>Z. angew. Chem.</i> , 41, 853–856 (1927).
Hydrogenation of castor oil; T. 270–290°; time 15–30 min.	0.5–1.0% WO <sub>3</sub> .	Grün and Czerny.
Hydrogenation of castor oil.	Oxides, sulfides, phosphates or silicates of Al, W, Zr, Mo, U.	I. G. Farbenindustrie A.-G.: E.P. 317,391, Oct. 9, 1929.
Hydrogenation of soy-bean oil with ethyl alcohol; T. 250°; time, 15 min.	Ni on kieselguhr.	Pastuscheni: <i>Masloboino Zhirovoe Delo</i> 1, 21–22 (1933).
Hydrogenation of sunflower oil to "Sealomas" (a method for determining activity of catalysts was proposed).	Ni.	Botkowskaja and Artamonov: <i>Vsesoyuz. Tsentral. Nauch.-Issledovatel. Inst. Zhirov (Trudy VNIIZh)</i> , 56–64 (1937).

Table 49 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of castor oil, cottonseed oil, etc. (a mixture of 70 per cent by weight of benzophenone and 30 per cent by weight of $\beta$ -naphthol); it is ascertained that the magnetic conversions of the catalyst influence the catalytic activity of the reaction not only in the case of reactions between gases as established for catalytic processes: $N_2O \rightarrow N_2 + 1/2 O_2$ (Refer to C. 1935 II 2174) $2CO \rightarrow CO_2 + C$ (Refer to C. 1936 I 6) $CO + 3H_2 \rightarrow CH_4 + H_2O$ (Refer to C. 1936 I 1366), but also in catalytic hydrogenation of unsaturated liquid cpds.	Ni-Cu (90-80 atom % Ni and 10-20 atom % Cu); Pd-Co (85 atom % + 15 atom %) (by a change of ferro-magnetism in the Curie interval the catalytic activity changes by an increase in the latter; however, in time the catalytic action decreases because the alloys are readily affected during the process).	Hedvall and Bystrom: <i>Z. physik. Chem. (B)</i> , <b>41</b> , 163-166 (1938).

Table 50. Catalytic Hydrogenation of Phenolic Oils.

Reaction	Catalyst	Observer
Hydrogenation of phenolic oils from low-temp. tars; fraction (b.p. 170-300°); T. 380-490°; varying pressure; yield, 14.2% gaseous hydrocarbons; fraction up to 170° best yield (20.1%) consisting of 65% aromatics, 33% saturated and 2% unsaturated hydrocarbons; a renewed hydrogenation of fraction at 170-250° gave 78.3% of an oil (b.p. 160-200°) consisting chiefly of hydroaromatic alcohols.	NiO.	Ando: <i>J. Soc. Chem. Ind. Japan</i> , <b>36</b> , 243B-244B (1933); <b>37</b> , 373 B (1934).
Hydrogenation of phenolic oils from low-temp. tars to benzine; higher initial pressures increased catalyst amount and higher reaction temp. favored hydrogenation.		Ando: <i>Ibid.</i> , <b>37</b> , 570B-573B (1934).
Hydrogenation of phenolic oils from low-temp. tars; in case of Mo contacts, addition of S caused an increase in the formation of light benzene because aromatic cpds. change into naphthenes.	MoO <sub>3</sub> (most active with respect to formation of low-boiling hydrocarbons); NiO and I; less active, Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , SnCl <sub>4</sub> .	Ando: <i>Ibid.</i> , <b>40</b> , 83B-85B (1937).

Table 51. Catalytic Hydrogenation of Camphor Oil and Turpentine Oil.

Reaction	Catalyst	Observer
Hydrogenation of camphor oil.	Metal layers on silica gel.	Morris and Reyerson: <i>J. Phys. Chem.</i> , <b>31</b> , 332 (1926).
Hydrogenation of turpentine oil to camphor.	Benzene, toluene.	Darasse and Dupont: <i>F.P.</i> 631,386, Jan. 28, 1927.
Hydrogenation of turpentine oil.	Catalyst prepared according to Russ. P. 23,523 (Refer to C. 1932 II 795).	Bag, Egupow and Wolokitin: <i>Russ. P.</i> 39,767, Nov. 30, 1934.

Table 52. Catalytic Hydrogenation of Heavy Hydrocarbon Oils.

Reaction	Catalyst	Observer
Hydrogenation of heavy oils to light oils; T. 250°; pressure, 20 atm.; time, 6 hrs.	Ni precipitated with Na <sub>2</sub> CO <sub>3</sub> + borax.	Müller: <i>F.P.</i> 520,180, June 21, 1921.
Hydrogenation of heavy mineral oils; T. greater than 300°.	Alkali metals, wood, coal, with coke powder added.	Erdöl und Kohle Verwertung A.-G.: <i>G.P.</i> 469,228, Kl 12o, Gr 1, Dec. 13, 1928. Grisard: <i>Swiss P.</i> 111,354, Sept. 1, 1925. I. G. Farbenindustrie A.-G.: <i>F.P.</i> 631,459, Dec. 21, 1927.

Table 52 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of heavy oils to light oils.	Halides of Al, Fe, Zn and Sb, also combined with an organic cpd., such as $\text{Al}_2\text{Cl}_3 \cdot \text{C}_6\text{H}_6$ (if the salts are insoluble in the oil to be hydrogenated, an oil in which they may be dissolved is added).	Société des Carburants Synthétiques: F.P. 39,983, Jan. 9, 1930. F.P. 607,155 (1925). (Refer to C. 1927 I 1105).
Hydrogenation of heavy mineral oils to light oils in two stages: (1) T. greater than $850^\circ\text{F}$ .; high $\text{H}_2$ pressure; (2) T. greater than $850^\circ\text{F}$ .; in a second container enriched in $\text{H}_2$ .	Cpds. of Cr and Mo together with Al and Zn and rare earths in fine suspension in the oil.	Standard Oil Development Co. (Gohr): E.P. 361,046, Dec. 10, 1931. E.P. 376,707, Aug. 11, 1932. U.S.P. 1,851,580, March 29, 1932.
Hydrogenation of heavy oils; pressure, greater than 56 atm.	$\text{AlCl}_3$ and hydrocarbons forming a double cpd.	Texas Co. (Behimer): U.S.P. 1,835,748, Dec. 8, 1931.
Hydrogenation of heavy hydrocarbon oils to light hydrocarbon oils.	Solid coking residues of fuels: wood, brown coal and pitch serve as catalysts.	Fedescra (France): F.P. 707,557, July 9, 1931.
Hydrogenation of heavy oils; hydrogenation products cracked into middle, light and heavy oils; process repeated several times; T. greater than $480^\circ$ ; pressure, greater than 20 atm.; temp. second stage hydrogenation, $315\text{--}425^\circ$ .	Catalysts stable to poisons.	International Hydrogenation Patents Co., Ltd.: F.P. 722,518, March 17, 1932. F.P. 725,671, May 17, 1932.
Hydrogenation of petroleum oils to light hydrocarbon oils in the presence of $\text{H}_2$ ; T. $200^\circ$ .	Ni impregnated with Fuller's earth.	Gray Process Corporation (Gray): U.S.P. 1,878,580, Sept. 20, 1932.
Hydrogenation of heavy oils.	Se, Te and their compounds, or oxides of Ni, Co, Fe, Mo, and W.	Société des Carburants Synthétiques: F.P. 41,616, Feb. 15, 1933.
Hydrogenation of heavy hydrocarbon oils under pressure.	$(\text{NH}_4)_2\text{MoO}_4$ heated at $420\text{--}440^\circ$ in a stream of $\text{O}_2$ and then with a $\text{Na}_2\text{S}$ solution, solid $\text{Na}_2\text{S}$ added, and $\text{CO}_2$ led into the mixture until a precipitate is formed, acidified with $\text{H}_2\text{SO}_4$ and diluted with water; the separated precipitate is washed with $\text{H}_2\text{S}$ -water, dried at $60^\circ$ , and mixed with 5-20% Al—Fe or Cr oxide.	Lobus, Polosow and Feofilow: Russ. P. 42,982, May 31, 1935.
Hydrogenation and cracking of heavy oils; pretreatment of the initial substance suggested: (1) by oxidation with air (1 cc./5 Kg. oil) or weak oxidizing agents (dilute solutions of $\text{FeCl}_3$ , $\text{KMnO}_4$ , $\text{K}_2\text{Cr}_2\text{O}_7$ , or $\text{H}_2\text{O}_2$ ) at $100^\circ$ for 24 hrs.; (2) by heating the oil below its decomposition temp. with catalysts; (3) by addition of substances forming compounds with injurious ingredients, e.g., $\text{FeCl}_3$ , Hg or Pb acetate, Na borate; when phenols or carbonic acids are present, treatment with alkali is suggested.		International Hydrogenation Patents Co., Ltd.: F.P. 793,898, Feb. 3, 1936.
Hydrogenation of heavy oils under pressure; high yields for low-boiling hydrocarbons obtained.	Slag, obtained by refining Fe alloys containing 1-10% oxides of Cr, Mo, W, V, Ti, or Mn, in addition to 5-20% $\text{Fe}_2\text{O}_3$ , 10-70% $\text{SiO}_2$ and 5-50% oxides of the alkaline earth metals.	Standard Oil Co. (Indiana) (Plummer): U.S.P. 2,033,737, March 10, 1936.
Hydrogenation and cracking of heavy hydrocarbon oils with a high C content; heated in spirals to $480\text{--}500^\circ$ ; then coke is separated from the oil and the vapors fractionated; the high-boiling fractions are catalytically hydrogenated at a temp. greater than $400^\circ$ and under 100 atm. pressure; the hydrogenation product is fractionated under 20 atm. pressure; a sudden temp. increase is prevented by lowering the pressure considerably and rapidly at the moment of increase in temp., from 200 atm. to about 135-175 atm., and then permitting the pressure to rise gradually to the working pressure.		Standard Oil Co. (Ruttruff): U.S.P. 1,948,736, Feb. 27, 1934. Standard I. G. Co. (Christ): U.S.P. 1,951,725, March 20, 1934.

Table 52 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of liquid or melted heavy or medium hydrocarbons to benzine under pressure and in many stages; the volatile reaction products, as well as the hydrogenation gas, are drawn off; the high-boiling fraction is subjected to a two-stage destructive hydrogenation, and all reaction products of this step returned for hydrogenation with the hydrogenation gas of the first step.		International Hydrogenation Patents Co., Ltd.: F.P. 828,161, May 11, 1938.
Hydrogenation processes.	Pt—Ni and Mo.	Jiri: <i>Helm. Hornický Vestník</i> , 19 (38), 241–245, 267–270 (1937).

Table 53. Catalytic Hydrogenation of High-boiling Oils into Low-boiling Oils.

Reaction	Catalyst	Observer
Hydrogenation of high-boiling to low-boiling hydrocarbons.	Heated Fe filings.	G.P. 226,135, Kl 23b, Gr 1, Dec. 9, 1908. (Refer to C. 1910 II 1261.)
Hydrogenation of high-boiling to low-boiling hydrocarbons.	Volatile catalysts; AlCl <sub>3</sub> .	Gulf Refining Company (McDuffie and McAfee): U.S.P. 1,578,049, March 23, 1926.
Hydrogenation of high-boiling to low-boiling hydrocarbons, the vapors of which are passed at high velocity in a stream of restricted cross-sectional area through an elongated cracking zone in which they are heated above 540°.	Finely divided Ni, Pd, or oxides of Th, Zn, Fe.	Pure Oil Co. (Smith and Watson): U.S.P. 1,887,047, Aug. 11, 1932.
Hydrogenation of high-boiling hydrocarbon mixtures or middle oils; T. 420–480°; pressure, above 50 atm.	Sulfides of metals of the 6th to 8th groups, especially Mo, W, Cr, U or Re, and addition of 0.5–15% basic reacting substances, such as pyridine bases, NH <sub>3</sub> or alkalis, K <sub>2</sub> CO <sub>3</sub> , Li <sub>2</sub> CO <sub>3</sub> , gaseous or liquid bases.	International Hydrogenation Patents Co., Ltd.: F.P. 793,227, Jan. 20, 1936.
Hydrogenation of high-boiling oils, such as crude oil or tar oil from bituminous substances, e.g., a German crude oil is (1) cracked with the addition of water vapor; T. 300–500°; (2) hydrogenated; T. 500–550°; yield, 90% of a benzine boiling below 180°.	Al, MgO and molybdic acid. Al.	Gewerkschaft für Handel und Industrie: F.P. 822,597, Jan. 4, 1938.

Table 54. Catalytic Hydrogenation and Cracking of Oils.

Reaction	Catalyst	Observer
Hydrogenation and cracking of mineral oils to saturated benzine.	10% Cu + Zn or Cd with B, Cr, Si, Ti, V, Ta, Mo, W or Co, or crude cresol or bauxite.	I. G. Farbenindustrie A.-G.: E.P. 276,001, Aug. 11, 1929.
Hydrogenation and cracking of mineral oils or tar oils; T. 300–400°; low or high pressure.	Metals.	Melamid: F.P. 648,625, Dec. 12, 1928. F.P. 648,144, Dec. 5, 1928.
Hydrogenation and cracking of mineral oils.	Charcoal paste.	Zotos: E.P. 386,993, Feb. 23, 1932.
Hydrogenation and cracking of hydrocarbon oils in vapor phase; T. 600–800°.	Alloys of Sn and Fe; may contain Ni, Cr, Co.	Forwood: F.P. 736,853, Nov. 30, 1932.
Hydrogenation and cracking of hydrocarbon oils under H <sub>2</sub> pressure.	Electromagnetic high-frequency field.	Ionizing Corporation of America (Henry): U.S.P. 1,881,406, Oct. 4, 1932.
Hydrogenation and cracking of mineral oils; T. 400–550°; pressure, 20–1000 atm.	Oil-soluble cpds. of organic acids, or phenols with one or more metals of the 2nd, 6th and 8th groups, e.g., Mo, Zn, Cr and Co.	I. G. Farbenindustrie A.-G.: E.P. 364,785, Feb. 4, 1932.

Table 54 (Continued).

Reaction	Catalyst	Observer
Hydrogenation and cracking of oils.	Fe oxide with cement shaped into sticks (channels with holes formed on heating due to carbonization).	Gyro Process Corporation (Harnsberger and Smith): U.S.P. 1,873,707 (1932). U.S.P. 1,874,943 (1932).
Hydrogenation and cracking of oils.	Elements of the 3rd to the 5th groups, especially $H_2$ cpds. of As, Sb, Bi, B and Sn or Si or the halide cpds., such as $BBr_3$ , precipitated in a fine dispersion, in the absence of $O_2$ , on metal oxides, such as $CaO$ , $BaO$ or active charcoal, asbestos, graphite; e.g., a mixture of $H_2$ and $SiH_4$ (from Mg silicide decomposed by $HCl$ ) is led over $Al_2O_3$ at $500^\circ$ , forming a ppt. of elemental Si.	I. G. Farbenindustrie A.-G. (Mittasch and Zorn): U.S.P. 1,895,764, Jan. 31, 1933.
Destructive hydrogenation of hydrocarbon oils; temp. in the reaction space regulated by the ratio of fresh oil to back flowing oil; mixture of both oils is introduced through a heating spiral in the reaction zone.		Standard I. G. Co. (Harding): U.S.P. 1,948,378, Feb. 20, 1934.
Hydrogenation and cracking of oils in a dispersed state at $800$ – $1000^\circ F$ . under pressure; reaction vapors are fractionated.	Finely divided hydrogenation catalysts: Mn, Al, Fe, Zn, Sn, Co, Ni, Cr, their oxides and salts.	Universal Oil Products Company (Olsen): U.S.P. 2,023,205, Dec. 3, 1935.
Hydrogenation and cracking of middle oils (high-boiling fractions, b.p. $275$ – $325^\circ$ ) to S and phenol-free products; T. $400^\circ$ ; pressure, 200 atm.; the fractions up to b.p. $275^\circ$ forming phenol-free products are hydrogenated at $400^\circ$ under 200 atm. pressure.	W sulfide.  Mo-Zn.	International Hydrogenation Patents Co., Ltd.: F.P. 796,443, April 7, 1936.
Destruction hydrogenation of middle oils rich in phenol to low-boiling products; yield, 65%; the oil is divided into two parts: 30 and 70; smaller part treated at $420^\circ$ under 180 atm. $H_2$ pressure; 30% low-boiling products containing phenol and olefin-free products are obtained; higher-boiling fraction separated, together with the greater part, is led over the catalyst at $420^\circ$ under 200 atm. pressure.	$MoO_3$ —ZnO.  WS.	International Hydrogenation Patents Co., Ltd.: F.P. 800,229, June 30, 1963.
Destructive hydrogenation of hydrocarbon oils or coal oil emulsions; the mixture of oil and $H_2$ is heated in a heating spiral, decomposed in gas and liquid in a separator and only then is the oil led into many catalyst chambers from the top to the bottom in a stream opposite to that of $H_2$ ; $H_2$ separated is led into one chamber.		Standard Oil Co. (Price): U.S.P. 1,948,732, Feb. 27, 1934.
Destructive hydrogenation of tar oils containing polymerizable substances; before hydrogenation or cracking, polymerization with $H_2SO_4$ is started and the reaction products, either together or after separation, form in themselves valuable low-boiling substances which are subjected to destructive hydrogenation at high temp. and high $H_2$ pressure.		Gesellschaft für Teerverwertung: G.P. 636,576, Kl 120, Oct. 15, 1936.



Table 54 (Continued).

Reaction	Catalyst	Observer
Destructive hydrogenation of commercial Rumanian petroleum; results indicate that with increased pressure the total yield drops, but increases the yield in benzene and the content of aromatic hydrocarbon, while the content in unsaturated hydrocarbons decreases and that of naphthenes remains constant; above 300° the benzene yield increases with temp.	The sequence in which catalytic activity decreases: mixed catalyst-MoS <sub>2</sub> + MgO + Al <sub>2</sub> O <sub>3</sub> → MoS <sub>2</sub> → ; without catalyst → Fe <sub>2</sub> O <sub>3</sub> + Ni.	Căndea and Kühn: <i>Bull. sci. école polytech. Timisoara</i> , <b>8</b> , 72-79 (1938).
Pressure hydrogenation of Albany crude oil and its derivatives with special consideration of benzene for airplanes with octane number 77 which is free from S and unsaturated hydrocarbons; it has a high volatility and a vapor pressure of 0.3 kg./cm. <sup>2</sup>		Doldi: <i>Chimie &amp; industrie</i> , <b>20</b> , 530-535 (1938).
Destructive hydrogenation of heavy hydrocarbons (high-boiling substances, such as petroleum, bitumen, slate oil and their distillation products or residues) subjected in steps to pressure hydrogenation and the light hydrocarbon oils distilled off; hydrogenation conditions adjusted to properties of initial substances; very high yields in light oils, especially aromatic hydrocarbon oils, are claimed.	None.	Léopold: F.P. 829,317, June 20, 1938.
Refining hydrogenation of hydrocarbon oils; S-containing oils are hydrogenated at 150-400° and under 10-100 atm. pressure.	Cpds. consisting of alkali aluminates and sulfides of metals: Al, Fe, Cu, Mo, W, Co, Ni, Sb; especially active are catalysts containing sulfides of Al, Fe, or Sb.	Universal Oil Products Company (Ipatieff and Komarewsky): U.S.P. 2,145,657, Jan. 31, 1939.
Refining hydrogenation of petroleum distillates in vapor phase at about 350-450°; the disulfides of oils are converted into mercaptans and further into hydrocarbons and H <sub>2</sub> S.	Sulfides of the iron group especially active are cpds obtained from iron oxides treated with mercaptans; the catalysts show extremely high stability and make possible very high passage velocities with practically complete desulfurization (0.007% S) of benzene.	Standard Oil Co. of California (Lyman, Nichols and Mithoff): U.S.P. 2,143,078, Jan. 10, 1939.
Hydrogenation of petroleum from Boldesti in a rotating autoclave, the benzene yield increases with working temp.; at 450° and 275 atm. maximum pressure it is 62%; final state of the reaction obtained after 45 min.; increase of H <sub>2</sub> initial pressure causes stronger saturation of benzene without essentially influencing the yield.	MoO <sub>3</sub> favors H <sub>2</sub> saturation and decreases partially the yield of benzene.	Căndea and Kühn: <i>Petroleum</i> , <b>35</b> , 187-90 (1939).

Table 55. Catalytic Hydrogenation of Coal (Industrial Process).

Reaction	Catalyst	Observer
A first attempt to hydrogenate coal; T. 270°C.; yield, 60% hydrocarbon oils.	Hydriodic acid solution.	Berthelot: <i>Bull. soc. chim.</i> , <b>2</b> (11), 278 (1869).
Hydrogenation of artificial coal prepared by heating cellulose to 340°C. at 100 atm. pressure for 8 hrs.	Hydrated Fe <sub>2</sub> O <sub>3</sub> added in amount 5% of the coal; later used in Bergius process; T. 440-490°C., time, 2 hrs.	Bergius: <i>J. Soc. Chem. Ind.</i> , <b>32</b> , 462 (1913). Bergius: E.P. 18,232 (1914).
Hydrogenation of coal.		Bergius: <i>Brennstoff-Chem.</i> , <b>6</b> , 64 (1925).

Table 55 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of coal, tar and petroleum to low-boiling hydrocarbons.	Mo (or compounds) with oxides.	I. G. Farbenindustrie A.-G.: E.P. 247,583 (1925). E.P. 272,830 (1925). E.P. 274,401 (1925). E.P. 247,586 (1925). E.P. 249,501 (1925).
Hydrogenation of coal.	W (or compounds) with $\text{Cr}_2\text{O}_3$ .	I. G. Farbenindustrie A.-G.: E.P. 251,264 (1925).
Hydrogenation of coal.	S compounds.	I. G. Farbenindustrie A.-G.: E.P. 247,584 (1925). E.P. 272,831 (1925).
Hydrogenation of coal.	Hydrogenated anthracene.	Hofsäss: U.S.P. 1,711,499 (1926).
Hydrogenation of coal.		Société Internationale des Combustibles Liquides: F.P. 618,490 (1926).
Hydrogenation of coal in a finely divided state; pressure, at least 50 atm.	Elements of the 5th group together with Mg or its cpds.	I. G. Farbenindustrie A.-G.: E.P. 275,663, Oct. 5, 1927.
Hydrogenation of coal.	Sn, melted.	Trautmann: E.P. 261,987, Jan. 19, 1927.
Hydrogenation of coal.	Reducible oxides, such as Mo, W, Cr, together with activators: $\text{Al}_2\text{O}_3$ , $\text{MgO}$ , $\text{ZnO}$ and $\text{K}_2\text{CO}_3$ best for hydrogenation.	Taylor: <i>Proc. Intern. Conf. Bituminous Coal</i> , 1, 190-199 (1928).
Hydrogenation of solid and liquid fuels.	Fe, Mg, K, $\text{Cl}_2$ solutions, to which $\text{Na}_2\text{CO}_3$ has been added, used for impregnating solid fuels; for liquid fuels, the dry catalyst should be dissolved; addition of this mixture in air catalyzes completely.	Etienne, Marty and Hippolyte: F.P. 664,568, Sept. 5, 1929.
Hydrogenation of Fushun coal.	$\text{Fe}_2\text{O}_3$ .	Abe: <i>J. Soc. Chem. Ind. Japan</i> , 34, 500B-510B (1931).
Partial pressure hydrogenation of a coal that does not coke or one that cokes badly; T. 350-420°; pressure, less than 50 atm.	Elements of the 6th group, or Sn, e.g., Sn oxalate.	Imperial Chemical Industries, Ltd. (Holroyd): E.P. 379,755, Sept. 27, 1932.
Hydrogenation of coal finely powdered and mixed with heated oil to render it fluid.	Catalyst supported on narrow, superimposed canals or passages of a large surface through which the substances or gases are forced to pass continually in parallel streams.	Bindley Processes, Ltd. (Robinson): F.P. 734,210, March 25, 1932.
Hydrogenation of coal and its distillation products to obtain lubricants; high-valent lubricants obtained by polymerization of ethylene gas.	$\text{AlCl}_3$ .	Nash: <i>Colliery Guardian</i> , 144, 550-551 (1932).
Hydrogenation of fuels.	Mo; at 400° Mo is reduced in the presence of $\text{H}_2$ ; unsaturated and aromatic hydrocarbons on the one hand and $\text{H}_2$ on the other hand form, with the 3-valent Mo addition cpds. with increased reaction ability.	Courierade: <i>Ind. chim. belge</i> (2), 3, 53-64 (1932).
Hydrogenation of Fushun coal according to the Bergius process; T. 350°.	$\text{Fe}_3\text{O}_4$ only slightly reduced in a nitrogen atmosphere by nascent $\text{H}_2$ ; at 350° the $\text{H}_2$ atmosphere causes a partial conversion into $\alpha$ -Fe; at 500°, the $\text{Fe}_3\text{O}_4$ is completely converted into $\alpha$ -Fe.	Abe: <i>J. Soc. Chem. Ind. Japan</i> , 35, 411-415 (1932).
Hydrogenation of coal from the Ural Mts., in stages; the benzene fraction consisted of aromatics and naphthenes; yield 70-75% of the original substance; medium and heavy oil, without a catalyst, converted (65%), to a resin-containing berginise, b.p. 200-350°.	$\text{MoS}_2$ .	Djakow and Losowoi: <i>Khim. Tverdogo Topliva</i> , 5, 719-736 (1934).

Table 55 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of pea size coal mixed with mineral oil or tar oil; T. greater than 300°; pressure, greater than 10 atm. H <sub>2</sub> .	Globules of Zn or Fe.	Ultramar Co. (Bates): E.P. 402,846, Jan. 4, 1934.
Hydrogenation of coal, mineral oils, tar, phenols and unsaturated hydrocarbons containing S.	The reaction chamber is made of Cr-, Mo-, Al-, W-, V-, Co-, Mn-, or Ni-containing steel and covered with a corrosion-resisting Zn layer by treating with Zn vapor in the absence of O <sub>2</sub> but in the presence of inert or reducing gases, such as N <sub>2</sub> , H <sub>2</sub> , at a temp. above that for the liquefaction of Zn (600-900°).	International Hydrogenation Patents Co., Ltd.: F.P. 775,202, Dec. 21, 1934.
Hydrogenation of coal and mineral oils; T. 200-700°; pressure, 100-1000 atm.	CCl <sub>4</sub> , CHCl <sub>3</sub> , CHBr <sub>3</sub> , CHI <sub>3</sub> ; halide derivatives of benzene and NH <sub>4</sub> Cl; also metals Fe, Ni, Co, Zn, Al, Sn, Ag, brass, Al-brass.	International Hydrogenation Patents Co., Ltd.: F.P. 786,937, Sept. 14, 1935. E.P. 442,440, March 5, 1936.
Hydrogenation of coal.	Usual catalyst on a carrier, such as charcoal, bauxite, florida earth.	International Hydrogenation Patents Co., Ltd.: F.P. 777,147, Feb. 12, 1935. E.P. 422,892, Feb. 14, 1935. F.P. 779,872, April 13, 1935.
Hydrogenation of solid C-containing substances, such as coal, pitch, wood in paste form; T. 470°; pressure, 200 atm.; yield, 92.5% liquid substances containing 3.7% asphalt.	Before hydrogenation the substances are impregnated with a solution of a catalyst in an organic solvent: (1) the coal containing basic ingredients is neutralized with dilute H <sub>2</sub> SO <sub>4</sub> ; (2) a solution of molybdc acid in CH <sub>3</sub> OH is sprayed over so that the coal contains 0.02% molybdc acid; the dried mass is mixed with a heavy oil in the ratio of 1:1; organic acids, their anhydrides, such as acetic, amino acids, ketones and nitriles may serve as organic solvents.	International Hydrogenation Patents Co., Ltd.: E.P. 427,275, May 16, 1935. F.P. 778,674, March 22, 1935.
Hydrogenation of brown coal; T. 400-420°.	Sn oxyhydrate; as solvent is used: phenol, Tetralin, pyridine; the most suitable solvent is that obtained from the same coal formation.	Rapoport and Ssudsilowskaja: <i>Khim. Tverdogo Topliva</i> , 6, 736-749 (1935). Ssudsilowskaja: <i>Ibid.</i> , 6, 826-831 (1935).
Hydrogenation of coal.	Mineral ingredients of coal act catalytically (glowed ashes lose their catalytic properties); Ca(OH) <sub>2</sub> and K <sub>2</sub> CO <sub>3</sub> added to the ash-containing coal do not decrease the action of MoS <sub>3</sub> catalyst; Ca(OH) <sub>2</sub> and K <sub>2</sub> CO <sub>3</sub> added to ash-free coal decrease the activity of the most active hydrogenation catalyst, MoS <sub>3</sub> .	Rapoport and Chudjakowa: <i>Ibid.</i> , 7, 346-359 (1936).
Hydrogenation of brown coal (400 kg.) to light benzine (55 kg.), light oil (350 kg.) and NH <sub>3</sub> (5 kg.); pressure, 1000 atm. mixed gases: 75% H <sub>2</sub> , 20% N <sub>2</sub> , 4% CO and 1% CH <sub>4</sub> ; heating occurs not by direct heating of the tubes, but by radiation from the wall into which they have been built.	Suitable catalyst; brown coal led with high velocity in the form of a suspension.	Compagnie de Béthune: F.P. 793,310, Jan. 22, 1936.
Hydrogenation of solid C-containing substances; T. higher than 420°; pressure, 100 atm. H <sub>2</sub> ; powdered coal reduced to a paste with anthracene oil; less than 1 cubic meter H <sub>2</sub> per 1 kg. initial paste used.	Na or K compounds combined with Al, Fe, Sn, <i>e.g.</i> , Na aluminate.	Compagnie des Mines de Vicoigne (Noeux and Drocourt): E.P. 447,930, June 25, 1936.

Table 55 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of coal.	Before hydrogenation the coal is treated in one of two ways: (1) it may be impregnated with a solution of NaOH or Na <sub>2</sub> CO <sub>3</sub> ; (2) it may be treated with a solution of a soluble cpd. of Fe or Co or both, especially the bivalent metals, e.g., halides or sulfates, or with finely divided Fe (sponge Fe or Fe carbonyl) precipitated or obtained as reduced Fe from Fe oxide), mixed and treated with a base, especially alkali in dissolved form.	International Hydrogenation Patents Co., Ltd.: F.P. 793,108, Jan. 16, 1936. Aust. P. 23,639 (1935). N.P. 56,918, Aug. 10, 1936.
Hydrogenation of C-containing substances; T. 470°; pressure, 200 atm.; yield, 37% hydrocarbons of b.p. below 180°.	FeS precipitated from FeCl <sub>3</sub> with aqueous (NH <sub>4</sub> ) <sub>2</sub> S; treated at 200° for 3 hrs. with H <sub>2</sub> S in a reaction vessel.	International Hydrogenation Patents Co., Ltd. (Pier, Jacob and Simon): E.P. 444,779, April 23, 1936. F.P. 794,936, Feb. 28, 1936. Austrian P. 23,418, March 19, 1936.
Hydrogenation of coal under 10–200 atm. H <sub>2</sub> ; the coal is extracted with hydrogenated cpds., such as tetrahydronaphthalene.	Mo serves to maintain the hydrogenation degree of the solvent.	Gewerkschaft Mathias Stinnes: F.P. 797,264, April 23, 1936.
Hydrogenation of coal.	Mn, Fe, Ni, Co, or their oxides or sulfides treated with base-acting substances simultaneously with free halides, especially Cl <sub>2</sub> , hydrogen halide or cpds. producing it under reaction conditions, as well as NH <sub>4</sub> Cl or organic halide cpds.; as base substances may be used: alkali or alkaline-earth metals or their oxides, hydroxides, sulfides, carbonates; furthermore, organic bases, such as pyridine; the finely divided metal is treated with an aqueous alkali solution at high temp.	International Hydrogenation Patents Co., Ltd.: F.P. 795,349, March 11, 1936. E.P. 450,473, Aug. 13, 1936.
Hydrogenation of brown coal; T. 450°; initial pressure, 100 atm.; yield, 35.9% oil 51.2% oil 56.3% oil; coal free from ash, when hydrogenated, gave 46.5% residue, while coal containing ash gave 28.7%; the oil yield from ash-free coal was 26.1%, while the untreated coal gave 35.9%.	Ashes act strongly catalytically. Without a catalyst. Fe <sub>2</sub> O <sub>3</sub> . MoS <sub>2</sub> . 2% Fe <sub>2</sub> O <sub>3</sub> increased the oil yield by 4%; 5% Fe <sub>2</sub> O <sub>3</sub> gave 42.2% oil with ash-free coal; SiO <sub>2</sub> decreased coke formation in the presence of MoS <sub>2</sub> and increased the oil yield; CaO, SiO <sub>2</sub> and FeS <sub>2</sub> , added in amounts corresponding to the ash content, had no influence on the hydrogenation of ash-free coal.	Waiselberg: <i>Khim. Tverdogo Topliva</i> , 8, 232–246 (1937).
Hydrogenation of coal-oil mixtures in the form of a paste which can be pumped into a hot spiral; preheated at 450°; heated at 560° under pressure slightly in excess; yield, benzene (anti-knock) and coke with 5–10% volatile parts.	With or without catalysts.	Universal Oil Products Company (Egloff): U.S.P. 2,091,354, Aug. 31, 1937.
Hydrogenation of coal and coal-tar oils under conditions of turbulent streaming; T. 560°; pressure below 200 atm. H <sub>2</sub> ; yield, 18% light oil, b.p. below 200°; 30% middle oil, b.p. 200–310°; 20% heavy oil, b.p. above 310°; in a heavy oil containing 15% suspended coal a conversion into 80% oil and gas is possible in a reaction time of 5 sec.	Without catalysts; the use of Sn as a catalyst in the hydrogenation of coal in turbulent streaming has no advantage; likewise the action of an aqueous solution of (NH <sub>4</sub> ) <sub>2</sub> S and (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> to neutralize the tar acids has no effect.	Morgan and Veyard: <i>J. Soc. Chem. Ind.</i> , 57, 152–162 (1938).
Hydrogenation of C-containing substances by H <sub>2</sub> or H <sub>2</sub> -containing gases at high temp. and under pressure.	Zn, Cu, and SiO <sub>2</sub> containing dust (the catalyst is activated by the addition of mineral acids).	Ceskoslovenské Továrny na Dusíkaté Látky Akc. Spol.: Tschsch. P. 63,053, Dec. 25, 1938.

Table 55 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of Japanese coal (Harutori and Naihoro coal).	Halides, especially $\text{PbCl}_2$ , $\text{SnCl}_4$ , $\text{PbI}_2$ , $\text{SnI}_2$ , $\text{ZnI}_2$ , were more active than the oxides (best were $\text{SnO}_2$ and $\text{NiO}$ ); in the case of mixed catalysts, $\text{Ni}_2\text{O}_3$ , $\text{SnO}_2$ , $\text{Fe}_2\text{O}_3$ , increase the amount of oil; $\text{MoO}_3$ and $\text{Cr}_2\text{O}_3$ especially increase the amount of benzene; with $\text{Ni}_2\text{O}_3$ : $\text{Fe}_2\text{O}_3$ (2:1) and $\text{Ni}_2\text{O}_3$ : $\text{SnO}_2$ : $\text{Fe}_2\text{O}_3$ (1:1:1) equal actions as with $\text{Ni}_2\text{O}_3$ are obtained; among the halogenides, $\text{SnCl}_4$ , $\text{NH}_4\text{Cl}$ , $\text{CHI}_3$ , $\text{KI}$ show a strong activation action.	Kurokawa, Hirota, Fujiwara and Asaoka: <i>J. Fuel Soc. Japan</i> (2), 18, 31-36 (1939).
Hydrogenation of coal solutions. "Barsasser-Saproximit" coal dissolves in anthracene oil to 94-95% at 400-425° under 20-30 atm. pressure; optimum ratio coal: solvent=30:70; the solution contains 30% organic substances and is concentrated in vacuum to 60%; the conc. solution is especially suitable for hydrogenation, whereby 90-95% of various oils are formed and only the non-volatile remain (2.4%); thus this kind of coal is converted to 80% in liquid fuels.		Djakowa, Losowoi and Kardasewitsch: <i>Zhur. Priklad. Khim.</i> , 12, 545-54 (1939); refer also to 12, 555-62 (1939).
Hydrogenation of coal; T. 800°; 5 atm. pressure; gases of the methane series are obtained; the hydrogenation residue is converted with vapor and likewise air into water-gas, <i>e.g.</i> , half anthracite is heated to 800° under 50 atm. pressure for 90 minutes whereby 0.51 $\text{H}_2$ per gram coal is introduced; hydrogenation starts at 600°; gas developed between 700-800° is separately collected and consists of 35% $\text{H}_2$ , 60% $\text{CH}_4$ , besides a small amount of $\text{C}_2\text{H}_6$ and unsaturated hydrocarbons; 20 gallons of tar are thus obtained; the weight loss of coal is about 40%; if the gasification of the residue is conducted under pressure and great excess of vapor and with introduction of air then, after separation of $\text{CO}_2$ , a gas rich in $\text{H}_2$ (about 80%) is obtained which may be used as a hydrogenation gas in the hydrogenation stage; a part of the CO can be hydrogenated to $\text{CH}_4$ also, whereby the yield of $\text{CH}_4$ is increased; by a suitable choice of single conditions, it may be worked to the effect of obtaining a final gas with a definite heat value by hydrogenation of brown coal; hydrogenation starts at 400-500° and the gas obtained between 700° and 800° contains about 70% $\text{CH}_4$ by a weight loss in coal of 60%.		Institution of Gas Engineers and Dent.: E.P. 503,183, April 4, 1939. E.P. 503,158, April 27, 1939.

Table 56. Catalytic Pressure Hydrogenation of Coal and Other Fuels.

Reaction	Catalyst	Observer
Pressure hydrogenation of coal under 50 atm.	Ag, Au, Ru, Rh, Os, Pd, Ir, Pt or cpds. on carrier, magnesia or magnesite.	I. G. Farbenindustrie A.-G.: E.P. 275,670, Oct. 5, 1927. E.P. 295,587, Oct. 10, 1928.
Pressure hydrogenation of coal and its distillation products together with $\text{H}_2$ following removal of phenols and their cpds.	Oxides of metals (difficultly reducible metal oxides of various valences); catalyst applied should not be poisoned by S.	Krauch: <i>Petroleum Age</i> , 25, 699-706 (1930).
Pressure hydrogenation of fuels.	Re or its cpds. in a colloidal state <i>e.g.</i> , Re sulfide on active coal obtained by precipitation with $\text{H}_2\text{S}$ and acidified with $\text{H}_2\text{SO}_4$ ; solution of $\text{R} \cdot \text{ReO}_4$ .	N. V. de Bataafsche Petroleum Mij: E.P. 358,180, Oct. 29, 1931.
Pressure hydrogenation of fuels: crude petroleum in liquid phase; T. 790°F.; pressure, 100-200 atm.; $\text{H}_2$ heated at high temp. in isolated heated receivers.	Finely ground and suspended catalysts of the 2nd and 6th groups.	Standard Oil Development Co. (Russell): E.P. 359,661, Nov. 19, 1931.
Pressure hydrogenation of fuels.	S cpds. obtained from metals or their oxides by treatment with volatile S cpds. in the presence of $\text{H}_2$ or in a stream of $\text{H}_2$ to which $\text{H}_2\text{S}$ , $\text{CS}_2$ , mercaptans or thiophene has been added.	I. G. Farbenindustrie A.-G.: F.P. 38,949, Aug. 10, 1931. add to F.P. 616,237 (1927). (Refer to C. 1927 I 1915).
Pressure hydrogenation of fuels.	Cu is replaced by other metals in a Zn alloy, <i>e.g.</i> , an alloy of equal parts of Zn and Ni or of 15% Zn and 85% Fe for covering the high-pressure apparatus used.	I. G. Farbenindustrie A.-G.: F.P. 39,175, Oct. 8, 1931. add to F.P. 697,539 (1930). (Refer to C. 1930 I 3079).

Table 56 (Continued).

Reaction	Catalyst	Observer
Pressure hydrogenation of a sludge from powdered coal in oil; dispersion of coal obtained by passing through a sieve with at least 100 meshes per sq. cm. (colloidal dispersion in oil).	Catalytically acting planes arranged at a distance from each other and parallel to the streaming direction, <i>e.g.</i> , plates of Ag, Cu, Cd, Pb, Bi, Sn or other alloys such as Cu+Zn, Ag+Cr or, together with Fe, are built in at a maximum distance of 2.5 cm.; the metallic surfaces may be covered; also catalysts such as oxides of Mo, Cr, W, Mg, Zn and Al, or sulfides of metals of the 6th group.	Standard I. G. Co.: F.P. 715,243, Nov. 27, 1931.
Pressure hydrogenation of fuels; catalysts increase the hydrogenation velocity, also improve the type of product originating thereby.	A combination of the elements of the 6th group, especially Mo and W, have the greatest activity, this activity being increased by metalloids acting, <i>e.g.</i> , in the synthesis of $\text{NH}_3$ of high-boiling oils, which are divided into two divisions; the catalyst increases the cracking velocity of the high-boiling products by dispersing the gaseous hydrocarbons; the predominance of the hydrogenation of non-volatile substances and the diminution of the activity must be avoided.	Krauch and Pier: <i>Z. angew. Chem.</i> , <b>44</b> , 953-958 (1931).
Pressure hydrogenation of baked coal, ground fine and heated for a short time at 300-600°; volatile parts driven off quickly and the coal particles blown to large size globules; weak oxidizing atmosphere (smoke gas with 5% $\text{O}_2$ ); particles hydrogenated at 510° under 250 atm. pressure.		I. G. Farbenindustrie A.-G.: E.P. 363,040, Jan. 7, 1932. E.P. 718,180, Jan. 20, 1932.
Pressure hydrogenation of fuels in liquid phase.	Organic Sn cpds. such as oxalates, acetates, formates, or others not volatile at the temp. of the reaction or subjected to decomposition: Sn tetraphenyl.	Imperial Chemical Industries, Ltd. (Askey, Holroyd and Cochran): E.P. 363,445, Jan. 14, 1932.
Pressure hydrogenation of fuels; an especially good yield of light hydrocarbons obtained by the addition of 8 parts $\text{CS}_2$ to 100 parts residue.	Mo plus promoters: Si, B, Li, P and Ca as well as $\text{H}_2\text{S}$ or substances producing $\text{H}_2\text{S}$ .	Peoples Gas Light & Coke Co. (Griffith): E.P. 370,909, May 12, 1932.
Pressure hydrogenation of fuels.	Suitable catalysts are heteropolymer acids containing Mo or W as a trivalent central atom, <i>e.g.</i> , $\text{NH}_4$ decamolybdate: ( $\text{NH}_4$ ) <sub>2</sub> · $\text{Mo}_{10}\text{O}_{32}$ · 3 $\text{H}_2\text{O}$ ; $\text{NH}_4$ pentadecamolybdate: ( $\text{NH}_4$ ) <sub>2</sub> ( $\text{MoO}_3$ · 6 $\text{H}_2\text{O}$ ) <sub>11</sub> ; $\text{NH}_4$ phosphopentadecamolybdate: ( $\text{NH}_4$ ) <sub>2</sub> · $\text{PO}_4$ ( $\text{MoO}_3$ · 6 $\text{H}_2\text{O}$ ) <sub>11</sub> ; $\text{NH}_4$ silico-molybdate, $\text{NH}_4$ tungsten-molybdate, $\text{NH}_4$ chrom-hexamolybdate, $\text{NH}_4$ alumina-hexamolybdate; catalysts of this type are more active than the simple molybdenum compounds, <i>e.g.</i> , $\text{MoO}_3$ .	I. G. Farbenindustrie A.-G.: F.P. 725,070, May 7, 1932. E.P. 371,833, May 26, 1932.
Pressure hydrogenation of brown coal fractions containing phenol in the preparation of motor fuels; that part boiling between 170-200° is separated from the crude product by fractional distillation at 400-600° under pressure greater than 20 atm. $\text{H}_2$ ; aromatic and hydroaromatic hydrocarbons obtained.	$\text{MoO}_3$ .	Imperial Chemical Industries, Ltd. (Jones): E.P. 372,783, June 9, 1932.
Pressure hydrogenation of fuels in the absence of $\text{O}_2$ but in the presence of large amounts of $\text{H}_2$ ; T. 300-600°.	High-valent catalysts; sulfides of elements of the 2nd to 8th groups prepared by intensive action of S or bivalent S cpds., such as $\text{H}_2\text{S}$ , mercaptans, thiophenes, $\text{CS}_2$ or thio acetic acid, or by the decomposition of thio- salts.	I. G. Farbenindustrie A.-G.: E.P. 379,335, Sept. 22, 1932. F.P. 728,913, July 13, 1932.
Pressure hydrogenation of fuels in 3 stages: (1) in a liquid phase; pressure above 50 atm.; hydrogenation products separated; (2) small amount $\text{H}_2$ free from C-containing cpds. in liquid products obtained and led over catalysts in vapor phase; (3) high yields of light hydrocarbons obtained.	In all 3 stages, compounds of the 4th to 8th groups, as well as Zn and Cd, are used at temp. ranging from 300-600°.	I. G. Farbenindustrie A.-G.: E.P. 380,615, Oct. 13, 1932.

Table 56 (Continued).

Reaction	Catalyst	Observer
Pressure hydrogenation of fuels; fuels to be hydrogenated are led, together with $H_2$ , into a pressure chamber in such a way that the coal suspension or oil stream from the outside and $H_2$ from the inside are directed toward a porous wall where they react with each other under intermittent pressure, the hydrogenating gas being shunted back and forth through the porous wall and the hydrogenation products packed inside the hydrogenation space.	Porous ceramic mass containing Mo or W; infusorial earth upon which active Fe is precipitated.	I. G. Farbenindustrie A.-G.; E.P. 381,367, Oct. 27, 1932.
Pressure hydrogenation of fuels.	Mo and W.	International Hydrogenation Patents Co., Ltd.; F.P. 722,463, March 17, 1932.
Pressure hydrogenation of fuels.	Reaction may be started with oxides, hydroxides, carbonates or sulfides; excluded are cpds. of Fe; most suitable are sulfides of Zn, Cd, Mg, Ti, Cr, Mo, W, U, V, Mn, Co, Ni, Al; likewise with addition of boron sulfide; action of S cpds. takes place under 3-15 atm. pressure; ammonium <i>p</i> -tungstate treated with $H_2S$ up to 410° under 5 atm. pressure for 24-36 hrs. in the absence of air; tungsten sulfide (excellent catalyst for the hydrogenation of mineral oils) formed under 200 atm. pressure; disintegrated and heated in a stream of $H_2$ up to 430°.	I. G. Farbenindustrie A.-G.; E.P. 379,335, Sept. 22, 1932. F.P. 728,913, July 13, 1932.
Pressure hydrogenation of fuels; with mono-clinic tungsten disulfide a 20% higher yield of benzene is obtained than with the hexagonal crystalline sulfide.	Such cpds. of W, Cr, Mo, V which are pseudomorphous with compounds used for the preparation of catalysts, e.g., the monoclinic needles of ammonium <i>p</i> -tungstate are treated with $H_2S$ for 48 hrs. at 300°; for 24 hrs. at 350°; for 48 hrs. at 410°; tungsten disulfide obtained is gray with a metallic sheen having the same needle crystalline structure as ammonium tungstate; the latter, treated in a similar manner, gives a crystallized oxide in blue-black needles; treating $MoO_3$ with $H_2$ for 15 hrs. at 230° gives pseudomorphous $MoO_3$ ; all these catalysts are suitable for cracking processes.	I. G. Farbenindustrie A.-G.; F.P. 735,295, Nov. 5, 1932.
Pressure hydrogenation of Or-containing fuels, such as brown coal or pitch, treated with heavy oils; T. 350°; pressure, above 100 atm. $H_2$ ; combined $O_2$ , $CO_2$ , or CO split off and the formation of not readily hydrogenated products avoided thereby.	Poison-stable catalysts.	International Hydrogenation Patents Co., Ltd.; F.P. 734,834, Oct. 28, 1932.
Pressure hydrogenation of coal distillation products in the preparation of aromatic hydrocarbons; water vapor may be added; T. 450-500°; benzene homologs chiefly obtained.	Fe, Ni, Cu, Co, Mn, Cr, Mo, Sn, Al with additions of alkali or alkaline earths, Si and B.	Greenstreet; Ital. P. 310,102, Oct. 26, 1932.
Pressure hydrogenation of baked coal; coal separated from its ash, ground to a very fine powder, pressed through a sieve, mixed with an adsorbent such as active coal or ash, and acted upon with a solvent.	Al molybdate solution used for impregnating coal.	I. G. Farbenindustrie A.-G.; F.P. 736,863, Nov. 30, 1932.
Pressure hydrogenation of coal or oil suspensions of coal such as mineral oils or tar; T. 230°; pressure, up to 3.5 atm.; a low boiling liquid hydrocarbon results.	Fe oxide containing Ti as it is obtained in the production of bauxite; contact mass consists of monazite, sand, Co, Ni, Cu, $Ce_2O_3$ , $Cr_2O_3$ .	Shering-Kahlbaum A.-G.; F.P. 739,770, July 7, 1932.
Pressure hydrogenation of liquid and solid fuels; initial substance in the first stage treated at 400-450° under 50-200 atm. $H_2$ pressure; hydrocarbons obtained; above 200° these hydrocarbons are recirculated in the reaction chamber and completely saturated with $H_2$ ;	Catalysts which act readily as hydrogenators, such as sulfides of heavy metals; oxides of the 3rd, 5th or 6th group on active carbon or $SiO_2$ .	I. G. Farbenindustrie A.-G.; F.P. 738,368, Dec. 24, 1932.

Table 56 (Continued).

Reaction	Catalyst	Observer
benzene is obtained and hydrogenated at 500–600° under partial pressure (less than 20% is maintained); a benzene of high anti-knock value results.		
Pressure hydrogenation of fuels such as coal, pitch, heavy oil, or distillates or residues of petroleum; heated with a catalyst in two stages: (1) to expel water at 100°; (2) to heat in retorts (coke oven type) at 1000–1500° for 24 hrs. H <sub>2</sub> is formed through chemical reaction and it in turn hydrogenates the reaction product; at the end of the hydrogenation process the contents of the retort are ignited by the introduction of air and the porous mass remaining impregnated with a salt solution and mixed with fuels.	Bauxite, infusorial earth, metal oxides, zinc dust, aluminum hydrosilicate, and such substances which develop H <sub>2</sub> by heating, e.g., MgCl <sub>2</sub> , carnallite, NaHSO <sub>4</sub> , NaOH (the latter together with Zn or Al dust).	Kern: U.S.P. 1,852,709, April 5, 1932.
Pressure hydrogenation of coal; preheating the so-called liquid coal to about 10° above its decomposition temp. (not above 470°) in absence of H <sub>2</sub> and O <sub>2</sub> -containing gases; in addition, the coal is treated with oil and hydrogenated. CO <sub>2</sub> , CO and S being split off.	MoO <sub>3</sub> .	British Colliery Owners Research Association (Graham and Skinner): E.P. 387,415, March 2, 1933.
Pressure hydrogenation of fuels.	Oxides or sulfides of W and U obtained from solutions by precipitation in a chemically active form, e.g., ammonium tungstate or ammonium uranate, mixed with HNO <sub>3</sub> and precipitated with an excess 1–4% free H <sub>3</sub> PO <sub>4</sub> ; the free metallic acids may be dissolved in conc. HCl or H <sub>3</sub> PO <sub>4</sub> and precipitated with NH <sub>3</sub> ; therefore an excess of 1–4% free acid remains; likewise, the sulfides are precipitated from a solution of ammonium salts or the free acids in H <sub>3</sub> PO <sub>4</sub> by introducing H <sub>2</sub> S.	International Hydrogenation Patents Co., Ltd.: F.P. 746,374, May 27, 1933.
Pressure hydrogenation in the preparation of anti-knock fuels; oils of an aliphatic character are converted by heating to a temp. less than 500°, with or without H <sub>2</sub> , into middle oils of an unsaturated nature containing about 60–80% cyclic hydrocarbons; the latter, when treated with H <sub>2</sub> in the presence of catalysts, give hydrocarbons practically saturated with H <sub>2</sub> , boiling at less than 250°; since these hydrocarbons contain the hydrogenating ring system, they are converted into anti-knock fuel by splitting off H <sub>2</sub> .	Catalysts which readily hydrogenate at 250°.	I. G. Farbenindustrie A.-G.: F.P. 739,988, Nov. 19, 1933.
Pressure hydrogenation of fuels; H <sub>2</sub> acts upon heavy oils at 400–500°; the reaction mixture is led in a streaming state through a high-pressure autoclave heated at 450°; light hydrocarbons are obtained.	Finely divided Fe in the presence of catalytically-active salts, such as those having an acid reaction, e.g., MgCl <sub>2</sub> , NH <sub>4</sub> Cl, CrCl <sub>3</sub> , NiCl <sub>2</sub> , MnCl <sub>2</sub> , or alkali borates; by the addition of MgCl <sub>2</sub> the yield of H <sub>2</sub> is considerably increased and the Fe converted into Fe cpds.	Uhde: F.P. 742,286, March 3, 1933.
Pressure hydrogenation of fuels; temp. controlled by means of thermo-elements; the hydrogenated oil is freed from ash and the asphalt is returned through narrow capillaries placed at varying heights of the contact space to a middle oil obtained by hydrogenation; the tubes and capillaries are washed with H <sub>2</sub> to prevent C precipitation and clogging.		Deutsche Gold und Silber Scheideanstalt (Roessler): E.P. 389,560, April 13, 1933.
Pressure hydrogenation of coal at 400° under high pressure for 3 hrs.; 93% of the C contained in the coal converted into liquid hydrocarbons.	(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> solution; 0.1% MoO <sub>3</sub> adsorbed by coal to be hydrogenated by impregnation with (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> , dried and mixed with a high-boiling oil containing 0.1% MoO <sub>3</sub> in the form of florida earth impregnated with (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> in a mixture of 4 : 1 ratio.	I. G. Farbenindustrie A.-G.: G.P. 570,951, Kl 12o, Feb. 22, 1933; F.P. 738,995, Jan. 4, 1933.



Table 56 (Continued).

Reaction	Catalyst	Observer
Pressure hydrogenation of fuels; T. 425°; pressure, 200 atm.; above 50% benzene boiling below 185° obtained; vapors of a middle oil led over the catalyst.	Halide cpds. of Mo, U, V; likewise with I <sub>2</sub> cpds. of Ag, Cu, Ti, Sn, Mn, Ni and Co and their mixtures on carriers, such as activated charcoal, silicic acid gel or pumice, <i>e.g.</i> , tungsten iodide.	I. G. Farbenindustrie A.-G.: F.P. 747,459, June 17, 1933.
Pressure hydrogenation of fuels.		A.-G. für Steinkohle-verflüssigung und Steinkohle-veredelung: F.P. 749,015, July 17, 1933.
Pressure hydrogenation of brown-coal tar or mineral oils; crude material containing cpds. with an alkaline reaction are neutralized with acids before hydrogenation begins.	Acid catalysts, such as organic sulfonic acid, together with metals of the 4th to 8th groups, or their cpds., or carbonic acids, such as formic acid, oxalic acid, acetic acid, as well as acid salts of Sn, Mo, etc., or oxygen acids, such as H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> .	I. G. Farbenindustrie A.-G.: F.P. 750,296, Aug. 8, 1933.
Pressure hydrogenation of fuels.	Metal salts of high molecular organic acids except salts of alkalis, alkaline earths, and noble metals, <i>e.g.</i> , Ni oleate, Co resinate, Mn laurate, Hg arsenate, Al palmitate and their mixtures.	Deutsche Hydrierung Werke A.-G.: F.P. 750,850, Aug. 19, 1933.
Pressure hydrogenation of coal or pitch.	Alkali or alkaline-earth metals or their mixture incorporated in the coal or pitch.	Compagnie des Mines de Vicoigne (Noeux and Drocourt): E.P. 768,351, Aug. 4, 1934.
Pressure hydrogenation of fuels.	Oxides or sulfides of metals of the 2nd, 4th and 6th groups of the Periodic System or their mixtures; especially suitable are oxides or sulfides of Cr, Mo, W mixed with oxides of Zn or Mg.	Standard I. G. Co. (Davis): U.S.P. 1,960,204, May 22, 1934.
Pressure hydrogenation of coal, coal distillates, mineral oils, cresols, etc.; T. 400-500°.	Mixtures obtained by combining sulfides of metals of the 6th group (Mo, W) with strong primary or secondary bases; the sulfides are dissolved in cyclohexylamine, piperidine or octadecylamine by heating; small amounts of S may be added.	Deutsche Hydrierwerke A.-G. (Rittmeister): G.P. 611,922, Kl 12o, April 9, 1935.
Pressure hydrogenation of C-containing substances, such as brown coal, pitch, torbanite (boghead coal), wood, and especially bituminous coal; T. 380-470°; pressure, 200-300 atm.; a considerable amount of heavy volatile oils obtained which, by renewed pressure hydrogenation, are converted chiefly into middle and light oils.	Sn oxalate or molybdic acid.	Imperial Chemical Industries, Ltd.: F.P. 775,721, Jan. 8, 1935. E.P. 425,679, April 18, 1935.
Pressure hydrogenation of carbonaceous substances; the amount of H <sub>2</sub> added is, in general, 400, 600, 1000, 2000 or more cc./ton of the C-containing substance.	Heavy metals of the 6th group of the periodic system, also Cr, U or their cpds., as well as Sn, V, Re, Mn, Zn, Cd, Al, or Co or their cpds. or oxides, hydroxides, sulfides of metals of the 6th group.	International Hydrogenation Patents Co., Ltd.: F.P. 765,923, June 18, 1934. E.P. 427,435, May 23, 1935.
Pressure hydrogenation of brown coal or pitch; T. 380-550°; pressure more than 20 atm.	Before hydrogenation the greater part of ash ingredients is removed by sedimentation or flotation; before or during hydrogenation treated with H <sub>2</sub> SO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub> or sulfonic acid.	International Hydrogenation Patents Co., Ltd. (I. G. Farbenindustrie A.-G.): F.P. 779,457, April 5, 1935. E.P. 428,749, June 13, 1935. Austrian P. 19,330/34, Sept. 26, 1935. Hung. P. 113,910, March 3, 1936.

Table 56 (Continued).

Reaction	Catalyst	Observer
Pressure hydrogenation of C-containing substances; electrolytic $H_2$ must be added only after heating the hydrogenation charge to the desired hydrogenation temp., or the treating of hydrogenation gas and hydrogenation charge should be undertaken in the presence of catalysts for the conversion of $O_2$ with $H_2$ to form $H_2O$ .	Ag—Cu or cpds. of the 7th or 8th group of the Periodic System, such as Co or Mn, which favor especially the conversion of CO with $O_2$ .	International Hydrogenation Patents Co., Ltd. (I. G. Farbenindustrie A.-G.); E.P. 465,413, June 3, 1935.
Pressure hydrogenation of fuels.	A fresh solution of $\frac{1}{2}$ mol $TiCl_3$ in benzene and one mol ammonium sulfotungstate is prepared with water, cooled, the precipitate filtered, washed with low-boiling solvents, such as acetone or alcohol, reduced with $H_2$ at 300–400°, and the gray-black mass molded by pressing; an aqueous solution of one mol cobalt chloride with a 5% aqueous solution of ammonium sulfotungstate may serve in preparing the catalyst; ammonium sulfotungstate and $FeSO_4$ , ammonium sulfovanadate and $NiCl_2$ , or ammonium sulfostannate and $FeCl_3$ in an alcoholic solution likewise may be used as a catalyst.	I. G. Farbenindustrie A.-G.; E.P. 434,141, Sept. 26, 1935. add to E.P. 379,335 F.P. 459,498, Jan. 1, 1936. add to F.P. 728,913 (Refer to C. 1933 I 545).
Pressure hydrogenation of fuels (high-boiling hydrocarbons, tars, mineral oils, pressure hydrogenation products or solid C-containing substances reduced to a paste with oil before heating); T. 400–500°.	2% catalyst to which S-containing hydrocarbons, such as $CS_2$ , are added.	International Hydrogenation Patents Co., Ltd.; F.P. 45,961, Jan. 17, 1936. add to F.P. 740,493 (1932). (Refer to C. 1933 I 4526).
Pressure hydrogenation of C-containing substances, such as coal or high-boiling oil fractions; if coal is the initial substance, the acid is added to the coal before charging it in the pressure chamber.	Pd or its cpds., e.g., oxides, sulfides, chromates, halogenides, acetates on carriers; acid reacting substances, acids of S or N, carbonic acids, sulfonic acids, acid phosphates or sulfates; the catalysts may contain also metals, e.g., Sn, Ge, Mo, Cr, W, Re, V, Fe, Al or their oxides, halides or sulfides.	International Hydrogenation Patents Co., Ltd.; F.P. 793,799, Jan. 31, 1936.
Pressure hydrogenation of carbonaceous substances; T. 380–550°; pressure, above 50 atm.	Pb salts (hydroxide, chromate, oxide), organic, carbonic or sulfonic acids except Pb oleate; Pb formate, acetate or oxalate in amt. 0.2–5.0%; in addition, acids carbonic or sulfonic, $HCl$ , $H_2SO_4$ or $HNO_3$ , or acid salts, e.g., acid phosphate, or acid sulfates of Sn, Mo, W, Mn, Re, Mg, Zn, Cd, Al, V, Cr.	International Hydrogenation Patents Co., Ltd.; F.P. 806,743, Dec. 23, 1906. F.P. 798,750, May 25, 1936.
Pressure hydrogenation of C-containing substances in a liquid phase.	Halides, hydrogen halides or non-metallic halide cpds. and catalytically active metals or their cpds.; to avoid accumulation of solid substances and thereby cause precipitation the supply of the catalyst is diminished from time to time; likewise the halide amount is increased.	International Hydrogenation Patents Co., Ltd.; F.P. 807,929, Jan. 25, 1937.
Pressure hydrogenation of coal.	A solution of a cpd., such as Mo, insoluble in $H_2O$ , also W, soluble in $H_2SO_4$ , is used to impregnate the initial substance; to the solution is added a wetting agent, such as isopropyl naphthalene sulfonic acid.	International Hydrogenation Patents Co., Ltd.; F.P. 809,398, March 2, 1937.
Pressure hydrogenation of solid or liquid C-containing substances, such as coal, tar, oils, especially brown coal.	$CaSO_4$ or Ca aluminate together with elements of the 6th to 8th groups of the Periodic System in amounts of 0.5–5.0%.	International Hydrogenation Patents Co., Ltd.; F.P. 812,218, May 3, 1937.

Table 56 (Continued).

Reaction	Catalyst	Observer
Pressure hydrogenation of solid C-containing substances, especially brown coal, to high-boiling oils; the residue is not returned as usual, but worked out by centrifuging.	0.2-4 parts aromatic light oils (b.p. not above 300°) added to coal paste; H <sub>2</sub> O content between 15-35% adjusted so that coal shows maximum adsorption ability; very fine grinding of coal required in order to disperse the catalyst thoroughly in the brown coal.	International Hydrogenation Patents Co., Ltd.: F.P. 812,219, May 3, 1937. F.P. 812,220, May 3, 1937.
Pressure extraction or mild pressure hydrogenation of coal; after separation of solid particles, gives Diesel and fuel oils with resin-like ingredients; treated at 20-100° with liquefied hydrocarbons having 1 to 3 C atoms; ingredients go into solution and after removal of the solvent serve to form a paste with the coal; the undissolved ingredients are mixed with middle oils of a cyclic nature and used as Diesel or fuel oils.		International Hydrogenation Patents Co., Ltd. (I. G. Farbenindustrie A.-G.): F.P. 816,371, Aug. 6, 1937. E.P. 469,048, Aug. 12, 1937.
Pressure hydrogenation of solid C-containing substances.	Zn salts of aliphatic monocarboxylic acids: acetic, propionic, butyric, and halides, H <sub>2</sub> halides or cpds. which under reaction conditions split off these cpds. such as hydrocarbon halides, SCl <sub>2</sub> , SCl <sub>4</sub> .	International Hydrogenation Patents Co., Ltd.: F.P. 807,936, Jan. 25, 1937. E.P. 816,955, Aug. 21, 1937.
Pressure hydrogenation of crude Fushun slate oil; T. 270-350°; initial pressure, 27-70 kg./sq.cm.; yield, 70 kg./sq.cm.; a temp. of 350° increased considerably the content of highly viscous oil and paraffin; by partial cracking at 320° under an initial H <sub>2</sub> pressure of 32 kg./sq.cm., 10% benzene and 2/3 of an amount of an initially contained paraffin were obtained.	Oxides of Ni, Mo, Fe, or Cr.  Mo oxide.  Mo—Cr or Fe oxide.	Kishi and Andô: <i>J. Soc. Chem. Ind. Japan (Supplement)</i> , <b>40</b> , 347B, 405B (1937).
Pressure hydrogenation of distillate and extraction products of coal.	Elemental S; the free S dissolves in the initial substances and is, therefore, active in an especially fine state of dispersion.	A.-G. für Steinkohle-verflüssigung und Steinkohle-veredelung (Moehre): G.P. 659,233, Kl 12o, April 28, 1938.
Pressure hydrogenation of C-containing substances, such as brown-coal tar, low-temp. tar and slate oil containing asphalt; T. 270°; pressure above 50 atm.; 90% asphalt substances converted; less than 5% gaseous products and less than 20% hydrocarbon oils boiling at 350°; products hydrogenated a second time at a higher temp.; dark in color; impure crudes converted into light yellow oils, such as gas oil, Diesel oil, lubricating oil.	Mixed catalysts; molybdic acid; ZnO and MgO pretreated with H <sub>2</sub> S.	International Hydrogenation Patents Co., Ltd.: F.P. 825,682, March 10, 1938.
Pressure hydrogenation of coal extracts; hydrogenated products show a very low asphalt content.	Mixtures of metal Fe, Fe oxides and Fe hydrates; either natural or artificial products, e.g., limonite or bauxite residues; the Fe content should be calculated as Fe <sub>2</sub> O <sub>3</sub> (50-60%).	International Hydrogenation Patents Co., Ltd.: F.P. 826,454, March 31, 1938.
Pressure hydrogenation and cracking of coal to aromatics, such as benzene or toluene; the heavy and middle oils are separated or split to lighter products and subjected to an aromatization at 500°; reaction products obtained fractionated to low-boiling aromatic hydrocarbons.		I. G. Farbenindustrie A.-G.: E.P. 482,431, April 28, 1938.

Table 56 (Continued).

Reaction	Catalyst	Observer
Pressure hydrogenation of coal extracts from brown-coal tar in liquid phase; T. 460–510°; pressure 100 atm. (30–60 atm.); aromatization of hydrogenation products, e.g. benzene.	Sulfides of the heavy metals, especially of the 6th group. 2 parts WS <sub>2</sub> to one part NiS.	International Hydrogenation Patents Co., Ltd.; F.P. 826,360, March 30, 1938.
Pressure hydrogenation of coal or brown coal; T. 330–400°.	Strong hydrogenating catalysts.	International Hydrogenation Patents Co., Ltd.; F.P. 825,687, March 10, 1938.
Pressure hydrogenation; the residue is regenerated by centrifuging of the chief mass from the oily parts, then distillation at low temp. and finally working out the mass to regenerate Fe in a blast oven or according to Renn's method.	Fe.	I. G. Farbenindustrie A.-G.; F.P. 831,384, Sept. 1, 1938.
Pressure hydrogenation of coal extracts (ash free substances) in liquid phase.	Powder-like catalysts (from the heavy hydrogenation products only the coarse parts of the catalyst are removed and replaced by a fresh catalyst in case of repeated hydrogenation); the used coarse grain catalyst is regenerated in the ordinary manner.	International Hydrogenation Patents Co., Ltd.; E.P. 493,947, Nov. 17, 1938.
Pressure hydrogenation of solid fuels; the coal pastes are hydrogenated in the usual way and then decomposed in a separator; the separation of hydrogenation products is undertaken in such a manner that the gas and vapor withdrawing products contain as much heavy oil as is newly formed in the process; from the middle oil obtained an amount corresponding to that for making up the paste is added to liquid residues, and this mixture is used to prepare a paste from the new material.		International Hydrogenation Patents Co., Ltd.; F.P. 833,774, Oct. 31, 1938.
Pressure hydrogenation of pressure extracts from coal, slate, or pitch to form antiknock benzene (the light parts are separated from the hydrogenation products and the heavy oils are led back into the hydrogenation zone and added to the fresh coal extracts without essential cooling).	Usual catalysts.	International Hydrogenation Patents Co., Ltd.; F.P. 829,291, June 17, 1938.
Pressure hydrogenation of C-containing substances to prepare hydrocarbon oils or waxes.	Mixed catalysts consisting of: (1) weak catalysts, cpds. of Mn, Fe, Cu, e.g., sulfides, phosphides or phosphates or their mixture; (2) strong catalysts, cpds. of Mo, Sn, W, Re, U, V, Cr, Ni, Co or their mixtures.	I. G. Farbenindustrie A.-G. and International Hydrogenation Patents Co., Ltd.; E.P. 488,651, Aug. 11, 1938. F.P. 830,135, July 21, 1938.
Pressure hydrogenation of young brown coal containing more than 20% O. (1) the coal pasted with heavy oil is preheated to about 440° in the presence of a small amount of H <sub>2</sub> ( $\frac{1}{4}$ – $\frac{1}{2}$ ) of the actual amount of H <sub>2</sub> used for hydrogenation); (2) then further addition of H <sub>2</sub> and likewise of catalysts follows and hydrogenation takes place at a temp. up to 475°; in this phase of the process the hydrogenation is carried out under pressures above 300 atm.		International Hydrogenation Patents, Ltd.; F.P. 830,493, Aug. 1, 1938.

Table 56 (Continued).

Reaction	Catalyst	Observer
Pressure hydrogenation of coal extracts (solid fuel, e.g., coal is extracted with decahydronaphthalene or other hydrogenated naphthalenes, likewise by addition of 10% pyridine under pressure and the content in S is removed by washing under pressure with an aqueous or alcoholic alkali solution; from the reaction products obtained the solvent is completely or partially distilled off and then subjected to a catalytic pressure hydrogenation).	As catalysts may be used, besides the usual substances which are stable to poisons, those whose activity has been disturbed by S, e.g., elemental Ni.	Dreyfus: E.P. 488,609, Aug. 4, 1938.
Pressure hydrogenation of coal, tars, asphalts and high-boiling mineral oils in the presence of naphthalene or tetrahydronaphthalene; naphthalene is hydrogenated during the hydrogenation process to tetrahydronaphthalene and this enables it to give off H <sub>2</sub> readily, so that it acts simultaneously as a good solvent and distribution agent, as well as a hydrogen transporter.	Stable to poisons.	Berl: E.P. 490,662, Sept. 15, 1938.
Pressure hydrogenation of coal; as dispersion medium for coal is used naphthalene; the process is led in 2 stages whereby in the first stage it is worked at comparatively low temp., and in both stages the same type of catalyst is applied.	A catalyst promoting the hydrogenation of naphthalene is used.	Gesellschaft für Teerverwertung m.b.H. (Weissgerber, H., Weissgerber, U. and Kaffer): G.P. 667,891, Kl 12o, Nov. 22, 1938; add to G.P. 638,637, Kl 12o Gr 1, July 28, 1937.
Pressure hydrogenation of coal, tars, and oils; (1) the initial substances are heated together with H <sub>2</sub> , whereby H <sub>2</sub> is dissolved in the initial substances under pressures of more than 500 atms., especially 1000 atms. and more, and at high temp.; (2) hydrogenation is then carried out essentially with H <sub>2</sub> dissolved in the above manner.	Ordinary catalyst.	I. G. Farbenindustrie A.-G. (Pier and Donath): G.P. 669,049, Kl 12o, Gr , Dec. 15, 1938.
Pressure hydrogenation of coal-oil pastes with more than 45% of solid coal; the thick paste is preheated to 280° and then heated to about 350° by mixing it with a heated coal-oil paste which contains less than 45% of solid coal; the mixture is then heated to the reaction temp. and hydrogenated as usual.		N. V. Internationale Hydrogeneeringsocctrooien Maatschappij: E.P. 495,954, Dec. 22, 1938.
Pressure hydrogenation of practically ash-free fuels, such as ash-free coal, tar, oil, or coal extracts in liquid phase.	Finely divided catalyst (the coarse grained catalyst particles are removed from the liquid products and replaced by fresh catalyst to effect regeneration).	International Hydrogenation Patents Co., Ltd.: F.P. 834,541, Nov. 23, 1938.
Pressure hydrogenation of brown coal or fat coal; reaction temp. is gradually decreased by 10-50°; asphalt-free oils or at least higher yield is claimed.		International Hydrogenation Maatschappij: F. P. 840,557, April 27, 1939; refer also to F.P. 839,663, April 7, 1939 and F.P. 838,765, March 15, 1939.
Pressure hydrogenation of brown coal; process carried out in two stages in the presence of catalysts promoting the hydrogenation of the addition substances, whereby in the first stage it is worked at comparatively low temp.	As pasting materials difficultly hydrogenated 3- and polynuclear hydrocarbons are recommended such as fluorene, phenanthrene, chrysene, Pyrene, naphthol fluorene; in the chief patent, tetrahydronaphthalene was used.	Gesellschaft für Teerverwertung (Weissgerber, H., Schulze, Kaffer and Weissgerber, U): G.P. 676,613, Kl 12o, June 8, 1939; add to G.P. 638,637 (1937).

Table 57. Destructive Catalytic Hydrogenation of Hydrocarbons.

Reaction	Catalyst	Observer
Destructive hydrogenation of hydrocarbons.	Ti, Zr, Nb, Ta, Th, U, Cu, Ti, as well as B, Si and other alloys.	I. G. Farbenindustrie A.-G.: E.P. 270,313, June 22, 1927.
Destructive hydrogenation of coal by heating under pressure.		Deutsche Bergius A.-G. für Kohle und Erdöl Chemie: G.P. 469,867, Kl 12o, Gr 1, Dec. 29, 1928.
Destructive hydrogenation of coal: a middle oil is led with H <sub>2</sub> at 450° under 200 atms. pressure, using WO <sub>3</sub> as a catalyst and treated primarily with NO at 350°.	Metals of the 6th group; catalysts heated for many hours before using at 300–600° in the presence of non-reducing gases, such as CO <sub>2</sub> , SO <sub>2</sub> , NO, O <sub>2</sub> , air, N <sub>2</sub> , MoO <sub>3</sub> and SiO <sub>2</sub> (with N <sub>2</sub> ) or CoO + Cr <sub>2</sub> O <sub>3</sub> (with CO <sub>2</sub> or Mo wire activated with NO).	I. G. Farbenindustrie A.-G.: E.P. 311,251, May 29, 1929.
Destructive hydrogenation for the production of hydrocarbon oils; a suspension of carbonaceous material in oil (particles passing through a 100-mesh screen) is led through a reaction zone packed with solid catalyst in lump form; pressure above 20 atms.; vapors condensed and recirculated in a definite manner; heavy oil and ash withdrawn; oil returned for preparation of the suspension.	Oxides of Cr, W and Mo with or without Zn, Al, or Mg oxides.	Standard I. G. Co. (Jennings): B.P. 365,892, June 23, 1930.
Destructive hydrogenation of fuels.	Mo polysulfide, especially MoS <sub>2</sub> , upon active charcoal as carrier; MoS <sub>2</sub> obtained in a finely divided state when (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> is precipitated with H <sub>2</sub> S and the ppt. treated with H <sub>2</sub> at 300–350°.	N. V. Bataafsche Petroleum Mij: F.P. 745,468, May 11, 1933.
Destructive hydrogenation of solid carbonaceous materials (fuels) suspended in or made into a paste with oil hydrogenated in liquid phase.	Catalysts consisting of a mixture of organic Sn, e.g., Sn oxalate, formate, acetate, citrate, etc.; Sn tetraphenyl and a cpd. of Cu and/or Fe obtained from Cu or Fe oxides in a finely divided state by an organic acid with precipitation of their salts on heating.	Imperial Chemical Industries, Ltd. (Somerset and Holroyd): B.P. 392,559, May 17, 1933.
Destructive hydrogenation of fuels; application of Bergius method in high-pressure hydrogenation of coal and tar; to offset poison effect of S, Fe oxide is added; C <sub>6</sub> H <sub>6</sub> yield increases with an increase in amount of S or S cpds.; formation of middle oil decreased in favor of the C <sub>6</sub> H <sub>6</sub> yield by the addition of S.	S-bound catalysts; Varge showed that when Mo, W, Fe, Ni, Co, are used the S content in the reaction system influences the yield and is therefore useful in catalysis.	Szeszich and Hupe: <i>Brennstoff-Chem.</i> , 14, 221–225 (1933).
Destructive hydrogenation of fuels; asphalt content of oils obtained by hydrogenation is considerably decreased and a high yield of light hydrocarbons results.	Metals, as well as their oxides and sulfides, especially of the 5th or 6th group; metallic halides, e.g., P, S, Se, Te, C, As, Sb, Ni, Si, also ethylene, benzene, chloroform, bromides, chlorides, HCl, HBr, Cl, Br.	I. G. Farbenindustrie A.-G.: F.P. 746,496, May 29, 1933.
Destructive hydrogenation of fuels.	Active charcoal the greater part of which has been freed from ash by acid treatment and impregnated with catalytically active metallic cpds., e.g., finely divided MoS.	N. V. Bataafsche Petroleum Mij: F.P. 745,074, May 2, 1933.
Destructive hydrogenation of brown coal.	Te compounds.	Rinse: <i>J. Soc. Chem. Ind.</i> , 51, 67–80 (1932). Rinse: <i>Chem. Weekblad</i> , 29, 42–43 (1932).
Destructive hydrogenation of coal; volatile products, such as phenols and neutral oils, removed from various cuts.	In presence or absence of catalysts.	Horton, King and Williams: E.P. 407,400, April 12, 1934.

Table 57 (Continued).

Reaction	Catalyst	Observer
Destructive hydrogenation of coal, oil and similar substances.	Water containing gel-like substances, bauxite, alumina, or silica gel heated to 450–650° and impregnated by catalytically active substances (regenerated after use by repeated heating in air, O <sub>2</sub> or O <sub>2</sub> -containing gases up to 450–600°).	King and Mathews: E.P. 410,771, June 21, 1934.
Destructive hydrogenation of high-boiling hydrocarbons; T. 750–950°F.; pressure, about 50 atm.	Cr—Mo.	Standard I. G. Co. (Peck): U.S.P. 2,009,717, July 30, 1935.
Destructive hydrogenation of coal: 90–97% Barsas coal; 92–93% boghead coal, and 81.09–83.77% Moscow brown coal; hydrogenation in two stages: (1) liquefaction at 400°; (2) cracking of the part boiling between 220–320°; yield of benzene and petroleum fraction: 67% from Barsas coal 58% from boghead coal 39% from Moscow brown coal.		Rapoport and Sscidsilovskaja: <i>Khim. Tverdogo Topliva</i> , 6, 40–66 (1935).
Destructive hydrogenation of coal, pitch and wood.	Catalysts colloiddally dispersed in the initial mass above 50°.	International Hydrogenation Patents Co., Ltd. (I. G. Farbenindustrie A.-G.): F.P. 777,119, Feb. 12, 1935. E.P. 431,435, Aug. 1, 1935. Austrian P. 19,038, Oct. 17, 1935.
Destructive hydrogenation of fuels.	Cr <sub>2</sub> O <sub>3</sub> and MgO mixed in equimolecular amounts with an aqueous solution of CrO <sub>3</sub> , moistened, ground and reduced in a stream of H <sub>2</sub> .	Polozow and Feofilow: Russ. P. 48,212, Aug. 31, 1936.
Destructive hydrogenation of bituminous coal; T. 410–480°; pressure 200 atm. H <sub>2</sub> .	0.2% PbCl <sub>2</sub> made into a paste, using oil; ratio, 1 : 1; before entering the reaction chamber, 0.5% PbCl <sub>2</sub> and 0.8% Cl (as CCl <sub>4</sub> ) is added; likewise, the halides of P, S, Se, As and Sb may be used.	International Hydrogenation Patents Co., Ltd.: F.P. 793,464, Jan. 25, 1936.
Destructive hydrogenation of fuels; in the apparatus, the corrosive-acting S-containing gases come into contact with parts covered with Cd alloys; the exposed parts are treated with Cd vapor at 700–900° in an atmosphere of H <sub>2</sub> for 24 hrs.	Catalyst composed of: 5.5% Cr, 1.6% Ni and 0.1% C, the remaining Fe being used as building material for the equipment.	International Hydrogenation Patents Co., Ltd.: F.P. 800,957, July 23, 1936.
Destructive hydrogenation of coal; gases formed by destructive hydrogenation of halogen cpds. substituted for coal are led into an alkali or an alkaline-earth solution, decomposed with a suitable aqueous solution of inorganic acids or their ammonium salts; the halide is converted into ammonium halide or hydrogen halide and added again to the initial material; 50 p. bitumen and 50 p. heavy oil are prepared with 0.4% NH <sub>4</sub> Cl and subjected to destructive hydrogenation; gases led into a suspension of lime in heavy oil; a CaCl <sub>2</sub> suspension is obtained, mixed in a mill with saturated (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> and the mixture used for further hydrogenation of new amounts of coal.		Imperial Chemical Industries, Ltd. (Matthews and Parsons): E.P. 440,456, Jan. 30, 1936.

Table 57 (Continued).

Reaction	Catalyst	Observer
Destructive hydrogenation of fuels; T. 350–370°; after 20–36 hrs., T. 400–420°.	400 g. $\text{H}_2\text{WO}_4$ under 12–15 atms. pressure mixed with 110 cc. liquid $\text{NH}_3$ and 280 cc. liquid $\text{H}_2\text{S}$ heated for 8 hrs. to 100° to form crystalline $(\text{NH}_4)_2\text{WS}_4$ which decomposes at 425°, giving an active catalyst ( $\text{H}_2\text{S}$ , $\text{O}_2$ -free).	International Hydrogenation Patents Co., Ltd.: F.P. 793,456, Jan. 24, 1936. E.P. 442,573, March 12, 1936.
Destructive hydrogenation of C-containing substances; clogging of the heat exchanger behind the reaction chamber by ammonium salts is prevented by the injection of water suspensions of naphthalene, anthracene, etc., by introduction of organic solvents.		International Hydrogenation Patents Co., Ltd.: E.P. 459,232, Feb. 4, 1937. F.P. 809,340, March 1, 1937.
Destructive hydrogenation of coal containing more than 82% C; pressure, more than 250 atms.; for each coal containing more than 82% C there exists an optimum hydrogenation pressure at which the same results are obtained as by hydrogenating C-poor coal at low pressure at 460°, e.g., the same results are obtained by hydrogenation of coal with 82% C at a partial $\text{H}_2$ pressure of 250 atms. as by hydrogenation of coal with 87% C at 500 atms.; for hydrogenation of coal with a C content between 82 and 88%, pressures of 350–650 atms. are applied.	0.06% Sn oxalate and 0.75% HCl.	International Hydrogenation Patents Co., Ltd.: F.P. 819,896, Oct. 28, 1937.
Hydrogenation of coal; destructive hydrogenation of goudron (reaction mechanism of hydrogenation).		Sinnatt, Williams and Cawley: <i>Congr. chim. ind. (Paris)</i> , 17, 476–486 (1937).
Destructive hydrogenation of Rumanian paraffins by heating in an autoclave at 350–450° without $\text{H}_2$ as well as with it in various amounts with and without catalysts; up to 400°, no essential changes are ascertained; simple cracking at 430° for one hour gives 20%, for 3 hours and likewise at 450° for one hour, 45% benzene (up to 150°); by destructive hydrogenation in one hour at 430° 21%; at 440°, 31%, and at 450°, 40% benzene is obtained over the catalyst; at 430°, 25%; at 440°, 38% benzene; the increased benzene yield by hydrogenation is obtained only in the presence of the catalyst at higher temperatures.	$\text{MoS}_3$ .	Candea and Saucine: <i>Petroleum</i> 34, No. 50, 1–5 (1938).
Destructive hydrogenation and cracking of hexadecane; normal or low molecular weight paraffins are obtained; hexadecane is prepared by hydrogenating hexadecene at 100–200° under high pressure; in the destructive hydrogenation of hexadecene the primary products are hydrogenated so rapidly that other reactions do not take place; however, the cracking products are partially aromatized or branched, indicating the existence of secondary reactions of the original unsaturated primary products; cyclization, polymerization and condensation reactions take place; from a comparison of other products with the $\text{CH}_4$ yield obtained by destructive hydrogenation, it may be concluded that the splitting of the hydrocarbon molecules proceeds only partially at the C–C bonds placed at the end, provided that the $\text{CH}_3$ first formed, as well as the $\text{CH}_2$ or $\text{CH}$ radicals, are not converted into higher hydrocarbons in the course of the reaction.	Ni-kieselguhr or $\text{Cr}_2\text{O}_3$ (essentially equal in action).	Waterman and Leendertse (Klijnsma and Suijders): <i>Trans. Faraday Soc.</i> , 35, 985–92 (1939).

Table 58. Catalytic Hydrogenation of Wood.

Reaction	Catalyst	Observer
Hydrogenation of wood; temp. (270–280°) below that at which exothermic cracking of wood takes place; hydrogenation continued until the greater part of the material is converted into a liquid or at least a plastic mass of oils and tars which are led away from the reaction chamber in a liquid state; $\text{H}_2$ and CO used for reduction.	Fe, Co, Ni, Cu, as well as their oxides.	Lindblad: Swed. P. 70,795, Dec. 16, 1930.
Hydrogenation of wood and pitch, also their conversion products; T. 350°; pressure, 40–100 atms.; eventually the material remains in a liquid state; alcohols, ketones and aldehydes are prepared.	Oxides, hydroxides or metal compounds not readily reduced under conditions of the reaction.	Lindblad: Swed. P. 71,841, May 19, 1931.
Hydrogenation of wood; tar, oil-like products and water separated; non-condensable gases returned to the reaction chamber.	Fe, Ni, or Co.	Lindblad: Swed. P. 72,646, Sept. 15, 1931.



Table 58 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of wood.	Cu.	Bergström: <i>Produkter ur trä</i> TVA, 1930-1932, Dec. 17, Kolnings Laboratoriet.
Hydrogenation of lignite at varying temp. under 300 atms. H <sub>2</sub> pressure for varying periods of time; lignite converted: 440°, 44.7% 460°, 40.4%, 1 min. 460°, 48.0%, 1 hr. 460°, 52.4%, 2 hrs. 480°, 53.2% density of oils obtained, 1.022 to 1.030.	Fe <sub>2</sub> O <sub>3</sub> (15% of the weight of lignite).	Pertierra: <i>Anales soc. espan. fis. quim.</i> , 31, 53-58 (1933).

Table 59. Catalytic Hydrogenation of Tar and Related Products.

Reaction	Catalyst	Observer
Hydrogenation of tar phenols.	Na formate.	Fischer and Schrader: G.P. 370,975, March 9, 1923.
Hydrogenation of coal-tar under pressure.	Catalysts applied in steps.	I. G. Farbenindustrie A.-G.: E.P. 320,673, Jan. 7, 1929. F.P. 663,539, Aug. 22, 1929.
Hydrogenation of tar; T. 450°; initial pressure 100 atms.	Mo.	Pier: <i>Iron &amp; Coal Trades Rev.</i> , 123, 705-709 (1931). Pier: <i>Chem.-Ztg.</i> , 56, 2-3, (1932).
Hydrogenation of tar and tar oils under pressure.	Mo and W in the presence of such amounts of H <sub>2</sub> S that will increase the action of the catalyst.	Deutsche Gold und Silber Scheideanstalt (Roessler): F.P. 711,046, Sept. 1, 1931.
Hydrogenation of tar for the production of secondary gasoline containing 50% unsaturated cpds. and 3.8% S under 80 atms. H <sub>2</sub> pressure; 380°, 36.7% S cpds. 400°, 70.2% 420°, 98.5% S cpds. 440°, 88.3%, no gum 440°, 99.6%.	MoO <sub>3</sub> .	Varga: <i>Math. naturw. Anz. ungar. Akad. Wiss.</i> , 48, 809-815 (1931).
Hydrogenation of low temp. tar and constituents, also neutral phenols, neutral oils and pitch.	CuO—MoO <sub>3</sub> .	Hlavica: <i>Chem. Obzor</i> , 5, 263-264, 266-288, 313-321 (1932).
Hydrogenation of tar oil constituents.	NaH; velocity in the formation of NaH is greatest at 300-310°; above 300° a hydride, Na <sub>2</sub> H <sub>2</sub> , less rich in H <sub>2</sub> is formed.	Hugel and Friess: <i>Ann. combustibles liquides</i> , 6, 1109-1147 (1932).
Hydrogenation of tar phenols to benzoic hydrocarbons.	NiO, MoO <sub>3</sub> , the latter being the more suitable.	Fischer, Bahr and Petrick: <i>Brennstoff-Chem.</i> , 13, 45-46 (1932).
Hydrogenation of low-temp. tar products heated in an autoclave; T. 320°; maximum pressure, 182 atms.; amount of resins and phenols considerably decreased; soluble phenolates, removed; neutral oils correspondingly increase reduction of phenols; non-resin phenols and neutral oils, when hydrogenated in the presence of MoS <sub>3</sub> (activity negligible), give light oils which are less affected than the resins of tar.	V <sub>2</sub> O <sub>5</sub> : 360°, 184 atms. MoO <sub>3</sub> : 300°, 180 atms. MoO <sub>3</sub> +S: 200°, 145 atms.	Morgan and Vinyard: <i>J. Soc. Chem. Ind.</i> , 51, 80-82 (1932).
Hydrogenation of coal tar or mineral oils under pressure to middle oils or benzine which are subjected to a pressure hydrogenation temp. ranging from 5° to 600°; products are essentially unsaturated hydrocarbons which may be polymerized into lubricants or alcohols or halide cpds.; lower hydrogenation temp. give products consisting of methane and its lower homologs.	A mixture of MoO <sub>3</sub> , CrO <sub>3</sub> and kaolin.	I. G. Farbenindustrie A.-G.: F.P. 721,718, March 7, 1932.

Table 59 (Continued).

Reaction	Catalyst	Observer
Hydrogenation of crude tar; T. 350°; initial pressure, 150 atms.; hydrogenation temp. without a catalyst 425° and an initial pressure of 100 atms.; low-boiling neutral oils little changed when hydrogenated with a catalyst; a large amount of viscous neutral oils formed at 300°.	1% (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> , Fe <sub>2</sub> O <sub>3</sub> ; reaction negligible at 300° and 350°.	Free: <i>Brennstoff-Chem.</i> , 13, 321-328 (1932).
Hydrogenation of tar in vapor phase under pressure; the vapors of substance to be hydrogenated with H <sub>2</sub> are led from below into a perpendicular reaction oven into which is introduced the finely divided catalyst passing over plates or falling into empty space.	MoO <sub>3</sub> -ZnO is suspended in the reaction space in which the oil evaporates immediately at the reaction temp.; the residue remaining drops upon plates deeply notched and arranged one on top of the other and kept in a constant rotating motion.	I. G. Farbenindustrie A.-G.: F.P. 718,956, Jan. 30, 1932.
Hydrogenation of coal-tar, oils and other bituminous substances in a finely divided state by a simultaneous action of CO and H <sub>2</sub> O vapor; T. 350-550°; pressure, less than 1 atm.; H <sub>2</sub> preheated; the crude coal may be distilled at temp. ranging from 350-550° in the presence of CO and with or without the addition of H <sub>2</sub> O vapor for purpose of hydrogenation; liquid fuels and low-boiling benzene obtained.	None.	Romwalter: Aust. P. 127,023, Feb. 25, 1932.
Hydrogenation of tar and tar-oil products under pressure.	H <sub>2</sub> MoO <sub>4</sub> .	Varga: <i>Math. naturw. Anz. ungar. Akad. Wiss.</i> , 50, 386-406 (1934).
Hydrogenation of tar or mineral oils.	Fe sulfide or cpds. readily converted into Fe <sub>2</sub> S <sub>3</sub> on hydrogenation; FeCl <sub>3</sub> solution precipitated with (NH <sub>4</sub> ) <sub>2</sub> S and the precipitated sludge treated with H <sub>2</sub> S at 200° for 3 hrs.	International Hydrogenation Patents Co., Ltd.: Ital. P. 334,639, June 24, 1935.
Hydrogenation of coal tar under 110 atms. pressure.	H <sub>2</sub> MoO <sub>4</sub> ; Si atoms added to activate the reaction.	Hollings and Griffith: <i>Proc. Roy. Soc. London (A)</i> , 148, 186-190 (1935).
Hydrogenation of the anthracene fraction of coal-tar under 300 atm. H <sub>2</sub> pressure; after 2 hrs., 22% light aromatic hydrocarbons were obtained; after three repetitions, a complete conversion (54%) into a readily boiling aromatic hydrocarbon, occurred; instead of pure H <sub>2</sub> , coking gas with H <sub>2</sub> was used, requiring five repetitions; the H <sub>2</sub> supply may be obtained wholly from gases formed.	MoS <sub>3</sub> .	Straler and Moissejenko: <i>Khim. Tverdogo Topliva</i> , 6, 161-171 (1935).
Hydrogenation of low-temperature tar; T. 300-510°; pressure, 200-400 atm.	Action of catalyst decreased the faster the higher the temp. used.	Sinnatt, King and MacFarlane: <i>Ind. Eng. Chem.</i> , 29, 133-40 (1937).
Hydrogenation of tar containing asphalt to lubricating oils; T. 400-485°; pressure 50 or more atm.; first freed from asphalt by treatment with liquefied low-boiling hydrocarbons, such as propane, at ordinary or increased temp. under pressure and then hydrogenated.	Halides of S, Se, Te, B, P or compounds splitting off hydrogen halides: CCl <sub>4</sub> , C <sub>2</sub> H <sub>5</sub> Cl <sub>2</sub> , NH <sub>4</sub> Cl, etc.	International Hydrogenation Patents Co., Ltd.: F.P. 816,885, Aug. 19, 1937. E.P. 469,158, Aug. 19, 1937.
Hydrogenation of bitumen and pyrolysis of natural gas; T. 425-450°; hydrogenation proceeds up to 50% yielding benzene and a small amount of coke; yield of oils from 1000 cu.ft. gas varies depending	(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> .	Mizuta: <i>Natl. Petroleum News</i> , 23, 89-96 (1931).

Table 59 (Continued).

Reaction	Catalyst	Observer
upon temp., velocity, duration of reaction; usually from 0.26-0.70 gallons, half consisting of light oils, 93.4% of which boil up to 150°; tar consists of high-boiling aromatic hydrocarbons from which 44% distilled up to 345°.		
Hydrogenation of pyrolytic tars containing naphthalene (the latter is hydrogenated to Tetralin and Decalin); H <sub>2</sub> originating by thermo-cracking is used.	Pt, Pd, Ni, and Co most active.	Smith, H. M., Kall and Grandone: U. S. Bur. Mines, Tech. Paper No. 587, 36 pp. (1938).
High-pressure hydrogenation of various tars; T. 450-480°.	MoO <sub>3</sub> .	Ando: <i>J. Soc. Chem. Ind. Japan</i> , 41, 247B-248B (1938); 41, 191B-193B (1938); 41, 292B-295B (1938).
Preparation of benzene and Diesel motor fuels; generator tar is mixed with kogasin whereby, as a result of the selective solubility of kogasin, two layers are formed; the lower layer contains hydrogen-poor aromatic and asphalt-like bodies, the upper non-aromatic, hydrogen-rich bodies dissolved in kogasin; the latter is hydrogenated in the gaseous phase, whereby on one side benzene and on the other side Diesel oil is obtained; the lower layer is hydrogenated in the liquid phase and converted into benzene and middle oil; the latter may be used as Diesel oil or converted by further hydrogenation (in the gaseous phase) into antiknock benzene.	Mo or Sn.	Uhde and Pfirrmann: E. P. 505,953, June 15, 1939. F. P. 841,528, May 22, 1939.

Table 60. Catalytic Hydrogenation and Cracking of Tars.

Reaction	Catalyst	Observer
Hydrogenation and cracking of tars.	Hydrides of alkali and alkaline earths; to prevent these metal hydrides from oxidizing, they are incorporated in a mixture or used in the presence of readily oxidized substances, such as hydroquinone, pyrogallol, iodine cpds., unsaturated organic chlorine cpds., amines, or ammonium iodide in the ratio of 1 : 1000 of the hydride.	Société d'Études Chimie Appliquée: G. P. 571,851, Kl 12o, March 6, 1933. G. P. 570,558, Kl 12o Gr 105, March 1, 1933.
Hydrogenation and cracking of hydrocarbon oils.		Standard I. G. Co. (Harding): U. S. P. 1,948,378, Feb. 20, 1934.
Hydrogenation and cracking of phenols from coal-tar fractions at 325° in continuous operation; T. 400°; pressure 40-150 atm. H <sub>2</sub> ; yield 56.68% phenol, 38.77% neutral oil; phenols to benzene, cresol to toluene.	MoS <sub>2</sub> , MoS <sub>3</sub> , Mo <sub>2</sub> O <sub>3</sub> .	Rapoport, Mintschenkow and Konow: <i>Khim. Tverdogo Topliva</i> , 6, 146-161 (1935).
Hydrogenation and cracking of peat tar.	MoS <sub>2</sub> .	Andrejewski, Diker, Mitkalew, Nemzow and Rysskin: <i>Ibid.</i> , 6, 926-942 (1935).
Hydrogenation and cracking of tars.	Glowed, grainy Al gel impregnated with (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> solution; after drying, the catalyst contains 25% (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> ; activity increased by preliminary heating for several hours in air at 500° due to the formation of Mo <sub>2</sub> O <sub>3</sub> ; preliminary heating under H <sub>2</sub> pressure decreases the activity; activation by H <sub>2</sub> S not required when tar contains sufficient S; activity of catalyst decreases on use.	King and Cawley: Dept. Sci. Ind. Research (Brit.), Fuel Research, Tech. Paper No. 41, 17 (1936).
Destructive pressure hydrogenation of tars or suspensions of brown coal, pitch, wood; 1000 atms. pressure (cooling system).		Société Belge de l'Azote et des Produits Chimiques du Marly & Société Chimique de la Grande Paroisse: F. P. 841,564, May 23, 1939. F. P. 841,565, May 23, 1939.

Table 60 (Continued).

Reaction	Catalyst	Observer
Berginization at low temp. of mazut (Jschimbajew) principally to unsaturated hydrocarbons; T. 420-460°; paraffins are readily cracked and aromatics are very stable; cracking products on the contrary show a paraffin character at 360-400° and elevated pressure; the cracking decreases and hydrogenation becomes stronger; aromatics, especially high molecular weight cpds., are readily hydrogenated and cracked; paraffins under these conditions are not readily cracked; cracking products show a more aromatic character; also, S cpds. are readily decomposed under these conditions.	10% MoS <sub>2</sub> .	Rutschkow and Nikolajewa: <i>Izvest. Akad. Nauk S.S.S.R.</i> , 171-184 (1937).

Table 61. Catalytic Hydrogenation of Cracking or Polymerization Products.

Reaction	Catalyst	Observer
Hydrogenation of hydrocarbons or cracking substances containing carbon.	Sulfides of heavy metals of the 5th and 6th groups: (1) a metal sulfide obtained by decomposing a S-containing salt at high temp. (300°); in preparation it is considered that no oxidizing substances are present. (2) O <sub>2</sub> -containing salts are treated during or after decomposition with S <sub>2</sub> or H <sub>2</sub> S. (3) metal sulfides prepared from C-containing salts of these metals, S <sub>2</sub> and H <sub>2</sub> S.	I. G. Farbenindustrie A.-G.; Polish P. 19,318, Feb. 17, 1934.
Hydrogenation of polymerization products of unsaturated hydrocarbons, e.g., propylene, butylene, amylene, in gaseous phase; pressure up to 30 atm.; hydrogenation is carried out in tube bundles and the pressure in the reaction tubes as well as that of both inlet and outlet, is kept separate.		International Hydrogenation Patents Co., Ltd.: F.P. 882,420, Dec. 30, 1937.
Hydrogenation of polymerization products of olefins, especially diisobutylene or isoheptylene, to the corresponding saturated hydrocarbons at 170-300° under normal or elevated pressure in two stages: (1) hydrogenation with refining. (2) hydrogenation with addition of an excess of H <sub>2</sub> ; between the two stages, the H <sub>2</sub> S formed is separated and the reaction product washed with water or dilute alkali; a cracking of the polymerizate, undesirable substances, and further polymerization, are prevented in this process.	Poison-stable catalysts, such as sulfides of the 6th group of the Periodic System. Ni (poison-sensitive catalyst).	International Hydrogenation Patents Co., Ltd.: F.P. 819,132, Oct. 11, 1937.
Hydrogenation of hydrocarbons in vapor phase, e.g., polymerization products of olefins are hydrogenated to high anti-knock benzenes; (this method is suggested also for hydrogenation of phenols).	A bundle of tubes charged uniformly with the catalyst; by using a built-in diaphragm at the opening of the tubes, a decrease in pressure is effected which is about 2-10 times as great as the pressure produced through the remaining contact tube.	International Hydrogenation Patents Co., Ltd.: Ital. P. 349,685, April 6, 1937.

Table 62. Catalytic Hydrogenation of Sulfur Compounds.

Reaction	Catalyst	Observer
Hydrogenation of CS <sub>2</sub> ; cracking of CS <sub>2</sub> takes place with formation of NiS and C at 350°; C formation in the reaction avoided by the presence of excess H <sub>2</sub> ; CS <sub>2</sub> considerably adsorbed on NiS <sub>2</sub> , but slowly a conversion takes place and the adsorbed amount is equal to the low value for NiS; the	NiS <sub>2</sub> ; pyrophoric Ni obtained by heating Ni(OH) <sub>2</sub> to 350° in a stream of H <sub>2</sub> ; SO <sub>2</sub> converts pyrophoric Ni into a mixture of sulfide and oxide, the presence of H <sub>2</sub> simultaneously reducing the oxide to Ni and the sulfide to NiS <sub>2</sub> ; contact with illuminating gas for a long time at 250° converts the pyrophoric	Griffith and Hill: <i>J. Chem. Soc.</i> , 1938, 717-720.

Table 62 (Continued).

Reaction	Catalyst	Observer
adsorption of CS <sub>2</sub> on NiS is considerable and reversible (at low temp. it is Van der Waals' adsorption); SO <sub>2</sub> is not adsorbed by NiS (above 300° an activated adsorption); on NiS <sub>2</sub> activated adsorption takes place at about 200°; CS <sub>2</sub> is adsorbed but little for all experimental temps.	Ni chiefly into Ni <sub>3</sub> S <sub>2</sub> ; Ni <sub>3</sub> S <sub>2</sub> for adsorption experiments prepared by heating NiS at 300° in a stream of H <sub>2</sub> for 3 hrs.	
Hydrogenation of simple S cpds., such as CS <sub>2</sub> and SO <sub>2</sub> ; T. 100-250°; the reaction is of the first order with respect to CS <sub>2</sub> ; at the beginning, with increasing CS <sub>2</sub> conc., it is greatly retarded; thus it is concluded that the reaction between CS <sub>2</sub> and H <sub>2</sub> proceeds stepwise, whereby the intermediate product is considered to be CH <sub>3</sub> SH; the adsorption of CS <sub>2</sub> is so great that the whole catalyst surface readily becomes covered, causing the reaction to slow down; this occurs even at high temp.; preparation of methyl mercaptan from equal volumes H <sub>2</sub> and CS <sub>2</sub> vapor; T. 250-300°; streaming velocity of 200 cm. <sup>3</sup> min.; H <sub>2</sub> S is separated from reaction products by means of Fe oxide; the CH <sub>3</sub> SH is condensed by means of solid CO <sub>2</sub> and acetone purified by fractionation.	Ni <sub>3</sub> S <sub>2</sub> (15 g.).	Crawley and Griffith: <i>J. Chem. Soc.</i> , 1938, 720-723.

Hydrogenation of SO <sub>2</sub> with dry H <sub>2</sub> ; T. 100-300°; H <sub>2</sub> S, but no S, formed; SO <sub>2</sub> is more strongly adsorbed on Ni <sub>3</sub> S <sub>2</sub> than H <sub>2</sub> which causes the reaction to slow down as in the case of CS <sub>2</sub> and H <sub>2</sub> ; thus the adsorption ability of one reaction partner is a disadvantage for the course of the reaction.	Ni <sub>3</sub> S <sub>2</sub> .	Crawley and Griffith: <i>J. Chem. Soc.</i> , 1938, 720-723.
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## PART XII

## Catalytic Dehydrogenation in Organic Chemistry

Table 1. Catalytic Dehydrogenation of Saturated to Unsaturated Hydrocarbons.

Reaction	Catalyst	Observer
Dehydrogenation of a gas consisting of 80% CH <sub>4</sub> and 6-7% C <sub>2</sub> H <sub>6</sub> to unsaturated hydrocarbons; T. 800°.	Charcoal, pumice and CuO, ratio 1 : 1 : 1.	Elworthy: <i>Trans. Roy. Soc. Can.</i> (3), 3, 16, 105 (1922).
Dehydrogenation of dicyclohexyl methane to fluorene and dicyclohexylketone to fluorene; T. 300°.	30% Pt charged on active charcoal.	Zelinsky, Titz and Gawerdowskaja: <i>Ber.</i> , 59, 2590 (1926).
Dehydrogenation of diphenylmethane to fluorene and diphenyl ethane to phenanthrene in a stream of weak CO <sub>2</sub> .	Pt, charcoal.	Zelinsky and Titz: <i>Ber.</i> , 62, 2869. (1929).
Dehydrogenation of ethane to ethylene; T. 600-900°.	Silicic acid.	Compagnie de Béthune: E.P. 308,200 (1929).
Dehydrogenation of saturated hydrocarbons to unsaturated hydrocarbons.		I. G. Farbenindustrie A.-G.: F.P. 624,980, July 30, 1927.
Dehydrogenation of saturated to unsaturated hydrocarbons; in converting mixtures of gaseous hydrocarbons into hydrocarbons less rich in H <sub>2</sub> at high temp., the original material is treated in stages at increasing temp. so that the hydrocarbons which do not at first participate in the reaction are converted in a subsequent stage at 1000°, and are later used in stages in which mainly hydrocarbons with two or more C atoms are converted above 1000°, principally CH <sub>4</sub> ; the thermal treatment is carried out in chambers provided with continuously or periodically heated heat exchanging filling material, such as coke or fire clay.		I. G. Farbenindustrie A.-G.: B.P. 364,106, Aug. 20, 1930.
Dehydrogenation of paraffinic hydrocarbons with at least four C atoms.	Silicic acid gel or Al gel covered with anthracite.	I. G. Farbenindustrie A.-G.: G.P. 565,159 (1932). E.P. 303,998 (1929).
Dehydrogenation of saturated to unsaturated hydrocarbons, chiefly ethylene and acetylene; T. 700° and 1000°.	Glowed coke covered with Ni, Cu or Pt oxides.	Konsortium für Elektrochemische Industrie: U.S.P. 1,898,301 (1933).

Table 1 (Continued).

Reaction	Catalyst	Observer
Dehydrogenation of saturated aromatic to unsaturated aromatic hydrocarbons, <i>e.g.</i> , (1) ethyl naphthalene to vinyl naphthalene; ethyl benzene to styrene; ethyl diphenyl to vinyl diphenyl; (2) isopropyl naphthalene to isopropenyl naphthalene and vinyl naphthalene; diethyl benzene to divinyl benzene; T. 300-600°; strongly diminished pressure.	Mixed basic catalysts: (1) Cu, Fe, Ni, on pumice; (2) $\text{CeO}_3 + \text{ZnO}$ .	Suida: Aust. P. 132,642, Feb. 25, 1933.
Dehydrogenation of $\text{CH}_4$ or its homologs to ethylene-containing gases; T. 450-650°.	Metals or oxides of metals, such as Ni, Co, Cu, or Zn, supplemented with an activator, <i>e.g.</i> , $\text{CaCO}_3$ , on a carrier like pumice.	Dreyfus: F.P. 749,916, Aug. 1, 1933.
Dehydrogenation of pressure hydrogenation products to aromatic hydrocarbons; T. 300-600°.	Active charcoal or cpds. of the 6th group, for example, $\text{MoO}_3$ , $\text{ZnO}$ , $\text{Al}_2\text{O}_3$ ; likewise mixed with $\text{CdS}$ , $\text{ZnS}$ , or $\text{Cr}_2\text{O}_3$ .	I. G. Farbenindustrie A.-G. (Mittasch, Pier, Wietzel and Langheinrich): U.S.P. 1,913,940 and 1,913,941, June 13, 1933.
Dehydrogenation of solid and liquid paraffinic hydrocarbons to higher olefins; T. 400-600°; time, 24 hrs.; yield, 95%, consisting of 70% $\text{H}_2 + \text{CH}_4 + \text{CO}_2$ .	Oxides of metals of the 5th to 7th groups, <i>e.g.</i> , $\text{VO}_3$ , $\text{WO}_3$ , or $\text{MnO}$ , $\text{ZnO}$ ; various reducing metals of the 3rd group, occurring in bauxite, with additions of Cu or Fe in $\text{NH}_3$ , for example, 50 parts $\text{Al}(\text{OH})_3$ , 40 parts $\text{ZnO}$ , 10 parts $\text{CaO}$ .	I. G. Farbenindustrie A.-G. (Wulff): G.P. 596,094, Kl 120, May 2, 1934.
Dehydrogenation of saturated hydrocarbons with two or more C atoms (without cracking) to olefins.	30% $\text{ZnO}$ mixed with 70% $\text{Cr}_2\text{O}_3$ .	Standard Oil Development Co. (Frolich and Boeckler): U.S.P. 1,944,419, Jan. 23, 1934.
Dehydrogenation of gaseous hydrocarbons of the paraffin series to olefins.	Highly active clay of the montmorillonite type.	Texaco Development Corporation (Halpern, Logan, Manley and Ulrich): Can. P. 342,155 (1934).
Dehydrogenation of hydrocarbon mixtures, such as paraffins: gaseous pentane to 20% pentene (480°), and decomposition products of coal; T. 400-600°.	Fuller's earth or silica gel charged with Co or Fe or metals of the 5th or 7th group of the periodic system, <i>e.g.</i> , a mixture of ammonium molybdate, cobalt nitrate and $\text{H}_3\text{PO}_4$ , precipitated on active charcoal.	I. G. Farbenindustrie A.-G.: F.P. 782,201 (1935). I. G. Farbenindustrie A.-G. (Pier and Donath): G.P. 578,567 (1933).
Dehydrogenation of saturated nitriles to unsaturated nitriles: propionitrile to propiolic acid nitrile; phenylacetone nitrile to phenylpropiolic acid nitrile and cinnamic acid nitrile; T. 400-800°; diminished pressure.	Graphite, charcoal, silicates.	I. G. Farbenindustrie A.-G.: F.P. 790,262 (1935).
Dehydrogenation of aliphatic hydrocarbons: pentane to 20% amylene.	Active charcoal; active silicic acid.	I. G. Farbenindustrie A.-G. (Krauch and Müller-Cunradi): G.P. 617,595 (1935).
Dehydrogenation of saturated higher hydrocarbons to olefins: ethylene; dilution with inert gases or an unsaturated hydrocarbon is recommended to bind the $\text{H}_2$ which is split off.	6-40% $\text{Al}_2\text{O}_3$ in a mixture with 15-25% $\text{Cr}_2\text{O}_3$ ( $\text{Cr}_2\text{O}_3$ precipitated from a solution on powdered or granulated $\text{Al}_2\text{O}_3$ ).	N. V. de Bataafsche Petroleum Mij.: F.P. 805,690, Nov. 26, 1936.
Dehydrogenation of saturated aliphatic hydrocarbons to hydrocarbons of the ethylene series.	Oxides of bi- or tri-valent Cr, alone or mixed with a carrier.	Uniesde Mell (Société Anonyme): F.P. 795,825, March 23, 1936.
Dehydrogenation of isobutane with $\text{H}_2\text{O}$ vapor and/or $\text{H}_2\text{S}$ , $\text{H}_2\text{Se}$ , or $\text{H}_2\text{Te}$ .	Active alumina with grain size of 8 to 14 mesh.	N. V. de Bataafsche Petroleum Mij. (Beeck, Groll and Burgin): E.P. 467,470, July 15, 1937. F.P. 814,712, June 26, 1937.
Dehydrogenation of propane to propylene; T. 400°; likewise, unsaturated hydrocarbons may be converted into saturated hydrocarbons by introducing $\text{H}_2$ .	Highly active chromoxide gel precipitated at 325-550° from a chromium nitrate solution by the addition of $\text{NH}_3$ and then dried.	Phillips Petroleum Co. (Frey and Huppke):

Table 1 (Continued).

Reaction	Catalyst	Observer
Dehydrogenation of aliphatic hydrocarbons with at least two carbon atoms, e.g., <i>n</i> -butane; T. 325°.	Cr <sub>2</sub> O <sub>3</sub> incorporated with stabilizing agents, e.g., difficultly reducible oxides: Al, Zr, Ti, Si, Th, B, or Mg, about 5% in amount, and 0.5-5.0% light reducible oxides of Te, Be, Pb, or Hg; the mixed catalyst is prepared by dissolving a Cr . . . salt and one or more salts of the above-named metals in water, precipitating the hydroxide by means of NH <sub>3</sub> , NaOH, or KOH, filtering, washing with water, and drying in air to a glassy, gel-like consistency.	Phillips Petroleum Co. (Frey and Huppke): U.S.P. 2,098,959, Nov. 16, 1937.
Dehydrogenation of aliphatic hydrocarbons.	Oxides of V, Ta on Al <sub>2</sub> O <sub>3</sub> ; Al <sub>2</sub> O <sub>3</sub> impregnated with NH <sub>4</sub> metavanadate or Al <sub>2</sub> O <sub>3</sub> mixed with Ta, Cr, Mo, or W oxides.	Universal Oil Products Co.: Ital. P. 351,120, May 21, 1937. Ital. P. 352,327, June 19, 1937.
Dehydrogenation (equilibrium) of <i>n</i> -butylene to butadiene $n\text{C}_4\text{H}_8 \rightleftharpoons \text{C}_4\text{H}_6 + \text{H}_2$	Cr <sub>2</sub> O <sub>3</sub> .	Dementjewa, Frost and Screbriakowa: <i>Doklady Akad. Nauk U.S.S.R.</i> , 15, 141-143 (1937).
Dehydrogenation of butane to unsaturated compounds, chiefly butylene; T. 480-600°; yield, 20-50%.	1% graphite + 2% B(OH) <sub>3</sub> added to a mixture consisting of 4% Cr oxide + 96% Al <sub>2</sub> O <sub>3</sub> (obtained through saturation of Al <sub>2</sub> O <sub>3</sub> with a solution of Cr nitrate); the mass is heated to about 180°, pressed into tablet form and reheated for 20 hours to 920°; thereby the resistance of these tablets increases from 16.8 kg./cm <sup>2</sup> to 91.0 kg./cm <sup>2</sup> .	Standard Oil Development Co.: F.P. 813,799, June 8, 1937.
Dehydrogenation of paraffin hydrocarbons; isobutane (gaseous) to isobutylene at high temp.	MgO, CrO <sub>3</sub> , ZnO; 90% MgO, 5% CrO <sub>3</sub> and 5% ZnO.	Universal Oil Products Company (Tropsch): U.S.P. 2,122,786, July 5, 1938.
Dehydrogenation of <i>n</i> -butane to butylene; T. 750-1380°; time, 40-20 as well as 3-20 sec.	Al <sub>2</sub> O <sub>3</sub> containing a chromite and a salt of an acid such as H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> or acetic acid, e.g., corresponding alkali salts or salts of Pb, Zn, Mg, Cd, Fe, Ni, Co as well as Pb chromate and ZnSO <sub>4</sub> .	Universal Oil Products Company (Tropsch): U.S.P. 2,122,787, July 5, 1938.
Dehydrogenation of isobutane to isobutylene or butane to butylene; T. 900-1000°F.; time, 3-20 as well as 3-6 sec.	Large amount of MgO and small amount of CrO <sub>3</sub> .	Universal Oil Products Company (Tropsch): U.S.P. 2,122,790, May 5, 1938.
Dehydrogenation of aliphatic hydrocarbons to unsaturated hydrocarbons (diolefins); T. 500-700°; contact time 0.1-0.2 sec.; diminished pressure; isobutane to 33% butylene, 35% and 33% H <sub>2</sub> ; T. 500-600°; contact time 4 sec.; from a mixture of $\alpha$ - and $\beta$ -butylene to 34% 1,3-butadiene; T. 600°; contact time 0.65 sec.; pressure 0.25 atm.; asym.-methylenelethylene and trimethylethylene (obtained from tertiary amyl alcohol) to 22% isoprene; T. 650°; contact time 0.65 sec.; pressure 0.25 atm.	Ti, Zr, Ce, Th and hafnium; Ti nitrate dissolved in cold water to form a saturated solution, 100 parts of which are added to 250 parts of active Al <sub>2</sub> O <sub>3</sub> obtained by calcining bauxite at 700° and forming grains of the order 3-5 mesh/cm. in size; this mass is dried for 2 hrs. at 100°; for 8 hrs. at 350° and finally treated with H <sub>2</sub> at 500°.	Universal Oil Products Co.: F.P. 822,520, Dec. 31, 1937. Ital. P. 351,947, April 29, 1937.
Dehydrogenation of hydrocarbons, for example, paraffin hydrocarbons, especially isobutane, to isobutylene; T. above 650°F., 900-1100°F. or 1150°F.; olefins, especially isobutylene, may be catalytically polymerized after S cpds., such as H <sub>2</sub> S, are converted by SO <sub>2</sub> and vapor into S and the latter removed; 94 parts by volume of isobutane and 40 parts by volume SO <sub>2</sub> are led over the catalyst after 1½ hours; the mixture contains 22.9% isobutylene.	Cr and Al oxide in the presence of SO <sub>2</sub> .	Standard Oil Development Co. (Rosen): U.S.P. 2,126,817, Aug. 16, 1938.

35 g. Al<sub>2</sub>O<sub>3</sub> and 25 g. Cr oxide (both calculated as nitrates) on white ware.

Table 1 (Continued).

Reaction	Catalyst	Observer
Dehydrogenation of low molecular paraffins to olefins; T. 585-650°; 0.1% water vapor required.	Activated $\text{Al}_2\text{O}_3$ catalyst prepared by dissolving Al in NaOH, precipitating with $\text{CO}_2$ and drying at 600°; large amt. $\text{Cr}_2\text{O}_3$ on $\text{Al}_2\text{O}_3$ used as carrier considerably decreases the reaction temp.; in this case, catalyst prepared by impregnating activated $\text{Al}_2\text{O}_3$ with a bichromate or chromic acid solution; large amt. alkali decreases activity of catalyst; if the catalyst becomes inactive by precipitation of coal it may be reactivated by heating to 600-700° in a stream of air.	Burgin, Groll and Roberts: <i>Natl. Petroleum News</i> , 30, 432-437, Sept. 7, 1938.
Dehydrogenation of hydrocarbons, e.g., paraffins, especially gaseous butane or pentane, to the corresponding olefins; T. 800-1200°F. (for 0.5-20 sec. action of the catalyst).	Nd-cpd., especially the oxide, in the presence of $\text{Al}_2\text{O}_3$ .	Universal Oil Products Co. (Murrell and Grosse): U.S.P. 2,148,129, Feb. 21, 1939.
Dehydrogenation of paraffin hydrocarbons to olefins, such as butylenes, propylenes, or ethylenes with $\text{MgO}$ ; T. 500°; ordinary or slightly increased pressure.	1-5% of a metal cpd., such as chromates, molybdates, aluminates, titanates, uranates, permanganates, or perhenates.	Universal Oil Products Co. (Tropsch): U.S.P. 2,148,140, Feb. 21, 1939.
Dehydrogenation of lower paraffin hydrocarbons.	Activated alumina.	Burgin, Groll and Roberts: <i>Oil and Gas J.</i> , 37, No. 17, 48-53 (1938).
Dehydrogenation of aliphatic hydrocarbons to the corresponding olefins and diolefins; process takes a few seconds at definite temp. and pressure; by further polymerization, they may serve as antiknock agents for mixing with benzene.		Universal Oil Products Co. (Grosse): Belg. P. 423,771, April 11, 1938.
Hydrogenation, dehydrogenation and reduction of hydrocarbons, e.g., conversion of butane to butylene and propylene.	The catalyst is led through the reaction zone and the temp. increased within the zone so that the reaction proceeds essentially uniform in all parts of the zone.	I. G. Farbenindustrie A.-G.: E.P. 500,366, March 9, 1939. F.P. 840,124, April 19, 1939.
Dehydrogenation of hydrocarbons, especially butane.	Mixture of $\text{Cr}_2\text{O}_3$ and amphoteric oxides, especially $\text{Al}_2\text{O}_3$ with small amounts of solid inorganic acid substances, especially boric acid, is heated to at least 875°; e.g., 4% $\text{Cr}_2\text{O}_3$ + 96% $\text{Al}_2\text{O}_3$ + 2% boric acid at 920°.	Standard Oil Development Co. (Sweeney and Spicer): U.S.P. 2,161,984, June 13, 1939.

Table 2. Catalytic Dehydrogenation of Cycloparaffins.

Reaction	Catalyst	Observer
Dehydrogenation of cyclohexane and alcohol; reaction not accelerated by exposure of the catalyst surface to ultraviolet radiation the amount of which is greater than that of the activation heat of the catalytic reaction; an inactive catalyst not activated by the action of light.	Pd with and without exposure to the radiation of a Hg cpd.	Balandin: <i>Z. physik. Chem. (B)</i> , 9, 319-328 (1930).
Dehydrogenation of cyclohexane to olefins and diolefins in the presence of water vapor; T. 650°; yield 90% olefins and 10% $\text{H}_2$ and $\text{CH}_4$ ; yield of butadiene, 60-70% of the theoretical.	Silica gel or $\text{Al}_2\text{O}_3$ covered with anthracite.	I. G. Farbenindustrie A.-G.: G.P. 535,726 (1931). E.P. 303,998 (1928).



Table 2 (Continued).

Reaction	Catalyst	Observer
Dehydrogenation of decahydronaphthalene, cyclohexane and piperidine; one and the same reaction gives the same activation heat for various cpds. on one and the same catalyst although, by using various catalysts for the various cpds., various activation heats are obtained.	Cu, Pt, Pd, Ni.	Adadurow: <i>Zhur. Fiz. Khim.</i> , <b>2</b> , 720-726 (1931).
Dehydrogenation of cyclohexane to benzene T. 500°.	Catalysts obtained by heating O <sub>2</sub> cpds. of Mo or W with NH <sub>3</sub> , or mixtures containing NH <sub>3</sub> , at ordinary or increased pressure, either alone or in mixtures with other catalysts (molybdates or tungstates of heavy metals, such as Cu, Ag, Fe, Ni), or on carriers.	I. G. Farbenindustrie A.-G.: G.P. 516,251, Kl 12, Jan. 22, 1931.
Dehydrogenation of cyclohexane; logarithmic relation between the components of Arrhenius' equation the result of which indicates that catalysts with high <i>Q</i> (active energy values) are the most active; in the catalytic dehydrogenation of cyclohexane, <i>Q</i> = 16,230 kg. cal./mol as compared with 9,850 kg. cal./mol for ordinary dehydrogenation, indicating that the difference is to be attributed to its affecting the Ni surface qualitatively and not merely increasing the surface area.	Ni; similar observations were made with TiO <sub>2</sub> ; neither effects the decomposition of CH <sub>4</sub> ; Ni on Al <sub>2</sub> O <sub>3</sub> approximates Pd on asbestos.	Balandin: <i>Z. physik. Chem. (B)</i> , <b>19</b> , 451-461 (1932); Roginskiand Rosenkevitch: <i>Chem. Abs.</i> , <b>25</b> , 2053 (1931); <i>Z. phys. Chem. (B)</i> , <b>10</b> , 49-85.
Dehydrogenation of cyclohexene to benzene by splitting of the ring to olefins, the latter changing to aromatic hydrocarbons above 700°; T. 500-750°	Silicic acid gel.	Maihle, Marty and Gaudry: <i>Compt. rend.</i> , <b>194</b> , 1947 (1932).
Dehydrogenation of cyclohexane to cyclohexene to hexene to olefins, the latter changing to aromatic hydrocarbons.	Silicic acid gel.	Maihle: <i>Chimie &amp; industrie</i> , <b>29</b> , 759 (1933).
Dehydrogenation of methylcyclohexane to toluene, T. 290-300°.	Charcoal impregnated with Pt hydrochloric acid (5.2 g. Pt adsorbed).	Packendorf and Leder-Packendorf: <i>Ber.</i> , <b>67</b> , 1388 (1934).
Dehydrogenation of methylcyclohexane.	Ni precipitated on Al <sub>2</sub> O <sub>3</sub> .	Balandin and Rubenstein: <i>Z. physik. Chem. (A)</i> , <b>167</b> , 431 (1934).
Dehydrogenation of 1,3-dimethylcyclohexane to <i>m</i> -xylene.		Balandin and Jurjew: <i>Zhur. Fiz. Khim.</i> , <b>5</b> , 393 (1934).
Dehydrogenation of methylcyclohexane.	Special Ni—Al <sub>2</sub> O <sub>3</sub> contact; double dehydrogenation velocity.	Balandin and Schujkin: <i>Ibid.</i> , <b>5</b> , 707 (1934).
Dehydrogenation of cyclohexane and methylcyclohexane to toluene; yield, 20% greater than cyclohexane to benzene at 200-270°; activation energy for both cpds. determined as 13,590 kg. cal./mol; methane, not above 2%, splits off.	Ni—Al <sub>2</sub> O <sub>3</sub> .	Balandin and Rubenstein: <i>Ibid.</i> , <b>5</b> , 12-19 (1934). Balandin and Rubenstein: <i>Z. physik. Chem. (A)</i> , <b>167</b> , 431-440 (1934). Balandin and Rubenstein: <i>Wiss. Werke Moskau. Mendeleeff. chem.-tech. Inst.</i> , <b>2</b> , 225-227 (1934).
Dehydrogenation of methylcyclohexane direct to toluene; T. 290-300°.	A typical hydrogenation catalyst should revert to a dehydrogenating catalyst by its poisoning effect; Pt precipitated on active charcoal (30 g. active charcoal stirred with a H <sub>2</sub> PtCl <sub>6</sub> solution containing 5.2 g. Pt) is an excellent hydrogenation catalyst, but does not dehydrogenate when poisoned with P (at 310°, benzene solution of PCl <sub>3</sub> dropped rapidly upon the catalyst); this catalyst does not hydrogenate benzene even at 220°, but does dehydrogenate cyclohexane directly to benzene;	Packendorf and Leder-Packendorf: <i>Ber.</i> , <b>67</b> , 1388-1391 (1934). Zelinsky and Borisow: (Refer to C. 1924 I 1142); <i>Ber.</i> , <b>57</b> , 150-53 (1924).

Table 2 (Continued).

Reaction	Catalyst	Observer
	the activity, not the difference in temp. is responsible for the occurrence of dehydrogenation and/or hydrogenation processes.	
Dehydrogenation of cyclohexane to benzene (splitting of the nucleus to a moderate extent); T. 500°.	$\text{Al}_2\text{O}_3$ ; $\text{Al}_2\text{O}_3 + \text{ZnCl}_2$ ; $\text{Al}_2\text{O}_3 + \text{H}_3\text{PO}_4$ ; addition of $\text{ZnCl}_2$ hinders the formation of decomposition products.	Karschew, Ssewerjanowa and Ssiowa: <i>Zhur. Priklad. Khim.</i> , <b>9</b> , 269 (1936). Karschew, Ssewerjanowa and Ssiowa: <i>Khim. Tverdogo Topliva</i> , <b>7</b> , 282 (1936).
Dehydrogenation of cycloparaffins to benzene; aromatic or saturated hydrocarbons may be added in vapor form; T. 200–300°.	Active charcoal and oxides of metals of the 6th group.	I. G. Farbenindustrie A.-G.: G.P. 626,273 (1936).
Dehydrogenation of cyclohexane mixed with $\text{H}_2$ to benzene; T. 550°.	Charcoal impregnated with $\text{K}_2\text{Cr}_2\text{O}_7$ .	
Dehydrogenation of cycloparaffins; T. 400–800°.	Porous charcoal and $\text{Al}_2\text{O}_3$ ; active charcoal alone or in a mixture with oxides of the third group.	I. G. Farbenindustrie A.-G.: F.P. 629,838 (1936).
Dehydrogenation of methylcyclohexane; T. 200–250°; activation energy, 12,000 cal./mol; methylcyclohexane dehydrogenates more readily than cyclohexane; reaction velocity determined by $\text{H}_2$ volume and refractometrically.	Ni on $\text{Al}_2\text{O}_3$ (obtained by stepwise reduction of the hydroxide mixture with $\text{H}_2$ at 250°, 270°, 300°, 330° and 350°, respectively, whereby it is reduced for each temp. until $\text{H}_2\text{O}$ formation is discontinued).	Balandin and Schujkin: <i>Uchenye Zapiski</i> , <b>6</b> , 281–286 (1936).
Dehydrogenation of cyclopentane and its homologs in a stream of $\text{H}_2$ to paraffinic hydrocarbons; the cyclopentane derivative with side chains, especially isoparaffinic hydrocarbons, is formed; T. 305–310°.	Pt.	Zelinsky, Kasanski and Plates: (Refer to C. 1933 II 2669); <i>Ber.</i> , <b>66</b> , 1415–19 (1933).
Dehydrogenation and cracking of ethylcyclopentane in the presence of cyclohexane as $\text{H}_2$ producing component to heptane; cyclohexane is dehydrogenated to benzene and nascent $\text{H}_2$ liberated, which causes ethylcyclopentane to split to heptane; the pentamethylene hydrocarbons under these conditions are not dehydrogenated, but decrease essentially the dehydrogenation of other hydrocarbons; by dehydrogenation of hydrocarbon mixtures (benzines), there is possibility of cracking cyclopentane due to the nascent $\text{H}_2$ formed, and the dehydrogenation of cyclohexane must be considered, because thereby the octane number of the dehydrogenated benzines is increased not only by aromatization, but also by the formation of isoparaffinic cpds.	Pt on active charcoal.	Zelinsky and Schachnasarowa: <i>Ber.</i> , <b>69</b> , 571–576 (1936).
Dehydrogenation of cyclohexane.	$\text{Cr}_2\text{O}_3$ .	Balandin and Brussow; <i>Zhur. Obshchei Khim.</i> , <b>7</b> , (69), 18–35 (1937).
Dehydrogenation of cyclohexane to benzene without secondary reactions; T. 330–460°; activation energy of the reaction is 8.6 kg. cal/mol.	Mutually precipitated $\text{Cu}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ in ratio of 1 : 4 (reduced in a stream of hydrogen).	Taylor and Joris: <i>Bull. soc. chim. Belg.</i> , <b>46</b> , 241–252 (1937).
Destructive dehydrogenation of cyclohexane to benzene accompanied by formation of considerable amounts of diphenyl; formation of <i>n</i> -hexane not observed; T. 330–375°.	Pt catalyst on charcoal.	Schujkin: <i>Zhur. Obshchei Khim.</i> , <b>7</b> (69), 1015–1021 (1937).
Dehydrogenation of methylcyclohexane and dimethylcyclohexane; T. 330–350° and 330°; accompanied by: (1) synthetic processes consisting in the formation of <i>p</i> -xylene from methylcyclohexane and xylene homologs from dimethylcyclohexane, and (2) destructive processes expressed in splitting off of the methyl groups from the initial hydrocarbon as well as dehydrogenation products; the destructive process predominates; the decomposition of considerable amounts of cyclohexene observed, as well as homologs over Ni catalyst, proceeds obviously through the formation of methylene groups, which are either hydrogenated to methane or used for methylation of aromatic hydrocarbons to the corresponding homologs.	Ni— $\text{Al}_2\text{O}_3$ .	
Dehydrogenation of cyclohexane; T. 350–450° 4 steps are distinguished in the course of the reaction: (1) activated adsorption of cyclohexane;	$\text{Cr}_2\text{O}_3$ and $\text{V}_2\text{O}_5$ .	Taylor and Yeddnapalli: <i>Bull. soc. chim. Belg.</i> , <b>47</b> , 162–171 (1938). Balandin and Brussow: (Refer to C. 1937 I 1911), <i>Z. phys. Chem.</i> (B), <b>34</b> , 96–120 (1936).

Table 2 (Continued).

Reaction	Catalyst	Observer
(2) dissociation into benzene and $H_2$ ; (3) desorption of benzene; (4) desorption of $H_2$ ; $Cr_2O_3$ , no marked high activity; activation energy, 24 kg. cal./mol; $V_2O_5$ , accounts for the activity of $Cr_2O_3$ ; a mixture of both oxides gives intermediate values for activities; the apparent activation energies are of the same order of magnitude as in the case of $Cr_2O_3$ .		
Dehydrogenation of 1-vinylcyclohexane-3 (a by-product in the manufacture of rubber) T. 300–320°; yield of ethylbenzene 78–84%; the part of styrene is insignificant.	Ni catalyst precipitated on $Al_2O_3$ .	Slobodin and Krassnobajewa: <i>Zhur. Obshchei Khim.</i> , <b>8</b> (70), 738–39 (1938).
Dehydrogenation of cyclooctene to styrene instead of cyclooctatetraene; T. 300°.	$Cr_2O_3$ .	Goldwasser and Taylor, H. S.: <i>J. Am. Chem. Soc.</i> , <b>61</b> 1260–63 (1939).
Dehydrogenation of cyclopentane to cyclopentadiene; vapors of cyclopentane are brought into contact with the catalyst at 500° and 0.25 atm. absolute pressure for 2 sec.; yield 35% of cyclopentadiene.	Granulated catalysts of active $Al_2O_3$ with small amounts of $Cr_2O_3$ , $V_2O_5$ , $MoO_3$ , or $MoO_2$ ; the catalysts are prepared by calcining bauxite, diaspor, and dawsonite ( $Na_2Al(CO_3)_3 \cdot 2Al(OH)_3$ ) and impregnating with about 4–10% of the corresponding oxides; 96% active $Al_2O_3 + 4\% Cr_2O_3$ .	Universal Oil Products Co. (Mavity and Morrell): U.S.P. 2,157,202, 2,157,203, 2,157,939, May 9, 1939.

Table 3. Catalytic Dehydrogenation of Heterocyclic Compounds.

Reaction	Catalyst	Observer
Dehydrogenation of hydrocyclic cpds. in mixtures with unsaturated systems and, at the same time, a reduction of unsaturated cpds., e.g., tetrahydro-isoquinoline with anethol in a xylene solution to isoquinoline at 149°; boiling one molecule of nicotine with two molecules of anethol in xylene at 150–152° results in the formation of nicotyrin (picrate at 164–165°).	Pd black.	Akabori and Suzuki: <i>Proc. Imp. Acad. (Tokyo)</i> , <b>5</b> , 255–256 (1930).
Dehydrogenation of hydrated heterocyclic cpds., such as 5,6- and 6,7-tetramethylene quinoline, results in a mixture of naphtho-quinoline and $\alpha$ -anthrapyridine; T. 400°; dehydrogenation succeeds also in a $N_2$ or $CO_2$ atm.	Metals of the 6th group or their cpds. with the addition of activators; pure molybdic acid; mixtures of ZnO and MgO pretreated with $H_2$ at 400°.	I. G. Farbenindustrie A.-G.: G.P. 579,146, Kl 12p. June 21, 1933. F.P. 744,595, April 24, 1933.
Dehydrogenation of heterocyclic cpds., such as piperidine, tetrahydroquinoline, decahydroquinoline, hydrogenated carbazene and indene.	Catalysts of heavy metals of the 6th group or stable cpds. thereof, such as oxides, sulfides, and selenides; catalyst may contain both activators and stabilizers.	I. G. Farbenindustrie A.-G.: Brit. P 387,507, Feb. 9, 1933.
Dehydrogenation of hydrogenated heterocyclic cpds., such as tetrahydrocarbazene (from phenylhydrazine and cyclohexanone), to carbazene.	Catalyst mixture consisting of: 8 parts by weight CuO 9 parts by weight $Cr_2O_3$ 2 parts by weight BaO 38 parts by weight Florida earth.	I. G. Farbenindustrie A.-G.: (Wulff and Breners): G.P. 579,146, Kl 12p., June 21, 1933.
Dehydrogenation of tetrahydrothiophene (thiophane) and other heterocyclic cpds. T. 400°; yield, 32%; *T. 350°; yield, 18%; side products: $H_2$ , $H_2S$ and saturated and unsaturated hydrocarbons, chiefly butylene and a small amount of butadiene.	20% Pt—charcoal; *NiS on $Al_2O_3$ (more destructive than Pt catalyst).	Jurjew and Borisow: <i>Zhur. Obshchei Khim.</i> <b>7</b> (69), 138–142 (1937). Jurjew and Borisow: <i>Ber.</i> , <b>60</b> , 1395–1398 (1936).

Table 4. Catalytic Dehydrogenation of Ethanol and Methanol.

Reaction	Catalyst	Observer
Dehydrogenation of ethanol with simultaneous formation of acetaldehyde.	Charcoal.	Lemoine: <i>Compt. rend.</i> , <b>144</b> , 357 (1907).
Dehydrogenation of alcohols to aldehydes or ketones (industrial process).	Cu, Zn, or brass.	Ipatieff:
Dehydrogenation of ethanol to acetaldehyde.	Ru and its cpds.; $V_2O_5$ , $UO_2$ , $MoO_3$ .	Badische Anilin- und Soda Fabrik: G.P. 275,518 (1913). Barrett Co.: U.S.P. 1,636,952 (1927).
Dehydrogenation of alcohols.	Cu.	Palmer and Constable: <i>Proc. Roy. Soc. London (A)</i> , <b>107</b> , 255-269 (1923).
Dehydrogenation of methanol.	$Al_2O_3$ .	Howard, Jr.: <i>J. Phys. Chem.</i> , <b>30</b> , 964-972 (1926).
Dehydrogenation of alcohols to aldehydes or ketones; T. 200-380°.	Cu+oxides of metals (Cr, Mn, Mg), or Cu+phosphoric acid salts [ $NaHPO_4$ , $Ba_3(PO_4)_2$ ]	I. G. Farbenindustrie A.-G.: E.P. 331,883 (1930).
Dehydrogenation of alcohols to aldehydes; T. 180-200°; yield, 88-92%.	Cu, Ag, Co or oxides of Zn or Mn; equal parts of Cu and Ag nitrate precipitated on silica gel; converted by heating at 250-300° into oxides, reduced in a stream of $H_2$ at 160-180°.	Société d'Etude Scientifique et d'Entreprises Industrielles: F.P. 707,132 (1931).
Dehydrogenation of ethanol in the presence of acetaldehyde; at 270°, the $CH_3CHO$ molecules remain on the surface 5 times longer than the $C_2H_5OH$ molecules, while at 240°, they remain 3 times longer than the $C_2H_5OH$ molecules (a method for determining the relative life on catalyzing surfaces).	Cu.	Balandin and Bork: <i>Wiss. Werke Moskau. Mendeleeff. chem.-tech. Inst.</i> , <b>2</b> , 217-220 (1934); refer also to <i>Trans. Leningrad. Chem.-Tech. Inst.</i> (1930-1933); Phys. Chem. Conference, Leningrad.
Dehydrogenation of ethanol with $NH_3$ to ethylamine; T. 300-400°; mixed catalysts Cr and Zn give as side products $\alpha$ - and $\gamma$ -picoline.	$Al_2O_3$ . $Al_2O_3 + Fe_2O_3$ $Al_2O_3 + Cr_2O_3$ $Al_2O_3 + SnO$ $Al_2O_3 + ZnO$ most favorably acting catalyst; 90% $Al_2O_3 + 10\% Fe_2O_3$ .	Schujkin, Balandin and Plotkin: <i>Zhur. Obshchei Khim.</i> , <b>4</b> , (66), 1444-1450 (1934).
Dehydrogenation of alcohols.	Alkali, alkaline earth or salts of heavy metals of Si (HF acid) melted together with 10% $H_3PO_4$ and boric acid (heated in vacuum until evaporation of $H_3PO_4$ ).	Plauson: G.P. 600,002, Kl 12o, July 13, 1934.
Dehydrogenation (mutual) of ethyl alcohol and aniline to form monoethylaniline; the substitution of $H_2$ in $NH_3$ molecules by the phenyl residue increases the reaction velocity of the mutual dehydrogenation with alcohol.	$Al_2O_3$ , pure; $Al_2O_3 + NiO$ .	Schujkin, Balandin and Dymow: <i>Zhur. Obshchei Khim.</i> , <b>4</b> , (66), 1451-1457 (1934).
Dehydrogenation of ethyl alcohol; T. 280-320°.	Cu; catalyst must be made passive toward side reactions with CO by addition of small amounts of Ag, etc.	Kagan: <i>Trudy Vsesoyuz. Mendeleevskogo S'ezda, 6th Congr.</i> , <b>2</b> (Part I), 739-745 (1935).
Dehydrogenation of primary alcohols to acids: acetic acid from ethanol; propionic acid from n-propanol; benzoic acid from benzyl alcohol.	Finely divided Cu, Ag, Co, Zn, Pd, or Pt metals taken in great excess and mixed with a catalytic base, e.g., partially hydrolyzable salt of an amorphous base or of Mg with an organic acid.	Hale: E.P. 427,631, May 23, 1935.
Dehydrogenation of alcohols to form esters (ethyl acetate); T. 250°; yield (once-through) 32%; the presence of water, acetic acid, or large amounts of acetaldehyde is injurious, while the addition of o-ethyl acetate and ethyl acetate is harmless.	Cu+0.2% Ce catalyst; highest degree of activity shown by it; $ZrO_2$ functions in both dehydrogenation and dehydration processes.	Dolgow and Koton (with Borisow and Nossowa): <i>Khim. Zhur., Ser. A.</i> , <b>6</b> (68), 1444-1451 (1936).

Table 4 (Continued).

Reaction	Catalyst	Observer
Dehydrogenation of unsaturated alcohols to unsaturated carbonyl cpds.; T. 500°; unsaturated alcohols of the formula:	Cu tube filled with brass.	Shell Development Co. (Groll); U.S.P. 2,011,317, Aug. 13, 1935.
$\begin{array}{c} \text{H} \\   \\ -\text{C}=\text{C}-\text{C}-\text{OH} \\   \\ \text{C}=\text{X} \end{array}$		
where X is H, or an alkyl, aryl, or aralkyl group; the free bonds may be occupied by H, alkyl, aryl, aryloxy, aralkyl, or aralkoxy groups which also may be substituted; T. 500°; for example: isobutanol to methyl acrolein and isobutyraldehyde; T. 285°; normal pressure; cinnamyl alcohol to $\beta$ - $\beta$ -dimethylacrolein and isovaleric aldehyde; T. 550°.	Brass.	
Dehydrogenation of absolute ethyl alcohol to esters (velocity 15 cc./hour for alcohol); T. 250°;	(1) Cu—Zr containing 0.9% Zr. (2) Cu—Ce containing 0.2% Ce.	Koton: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , 6 (68), 1291-1294 (1936).
(1) yield: 50.6% ethyl acetate (passing four times yielded 66.4% ethyl acetate) 3.0% acetic acid 6.0% acetaldehyde (2) yield: 33.0% ethyl acetate 6.0% acetic acid using 96% alcohol, after 162 hours the yield decreased 7-8% for the Cu—Zr catalyst.		
Dehydrogenation of alcohols to ethers and unsaturated hydrocarbons.	Waste products obtained from Al salts from clays by action of acids.	Daschkewitsch and Wolnow: <i>Russ. P.</i> 48,289, Aug. 31, 1936.
Dehydrogenation of alcohols of the series $\text{C}_n\text{H}_{2n-1}\text{OH}$ in the absence of organic acids to form by decomposition increased amounts of esters or acids.	Pure Cu activated by $\text{CeO}_2$ , $\text{ZrO}_2$ and $\text{Al}_2\text{O}_3$ .	Koton: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , 7 (69), 2188-2194 (1937).
Dehydrogenation of methanol to formaldehyde; T. 400-470°.	(1) Cu—Pb—Sn (best results, no fatigue); brass gauze, silver plated brass, and granulated Zn.	Plotnikow and Baljassny: <i>Ukrain. Akad. Nauk, Zapiski Inst. Khim.</i> , 4, 269-76 (1937).

Table 5. Catalytic Dehydrogenation and Catalytic Dehydration of Alcohols.

Reaction	Catalyst	Observer
Relationship between dehydrogenation and dehydration: practically independent of the structure of alcohol as compared with the dependence on the nature of the catalyst.	ZnO obtained from: (1) $\text{ZnSO}_4$ (2) commercial product (dry method) (3) Zn isopropoxide in moist air; the catalysts are suitable for: (1) dehydration (2) dehydrogenation (3) similar to (2) except in the case of ethanol.	Adkins and Lazier: <i>J. Am. Chem. Soc.</i> , 48, 1647-1677 (1926).
Dehydration of alcohols; a pure dehydration catalyst accelerates chiefly the H—OH recombination without influencing the combining of H—H, while a typical dehydrogenation catalyst insures H—H recombination; HCl more active than pure glass for H—OH recombination, but less active than clear glass by the Cl—Cl	$\text{Al}_2\text{O}_3$ accelerates greatly the H—OH reaction; on the contrary, $\text{Al}_2\text{O}_3$ and HCl ineffective for the H—H reaction; KOH and $\text{K}_2\text{CO}_3$ and especially Zn— $\text{Cr}_2\text{O}_3$ , as well as metal surfaces, are good agents for the H—H reaction.	Taylor and Levin: <i>Ibid.</i> , 52, 1910-1918 (1930).

Table 5 (Continued).

Reaction	Catalyst	Observer
Dehydrogenation and dehydration of alcohols.	Metal oxides or $\text{SiO}_2$ + basic substances suitable for dehydrogenation action; when acid substances are added the basic additions are oxides, carbonates, hydroxides or organic acid salts of alkali or alkaline-earth metals; acid additions are the oxides of Mn, S, Cr, P, As, Si, Ti, Sn, B, Al; oxide catalysts used as base substances may contain the oxides of Be, Mg, Zn, Al, Si, Ti, Ge, Zr, Sn, Ce, Th, V, Bi, Cr, Mo, W, U, Mn, Fe and the rare earths.	Dupont: E.P. 323,713, Feb. 6, 1930.
Simultaneous hydrogenation and dehydrogenation of a mixture of 2 parts cyclohexanol and 1 part phenol; T. 200°; quantitative yield of cyclohexanone.	Hydrogenation catalyst.	Schering-Kahlbaum: Swiss P. 141,528 (1930).
Parallel dehydrogenation and dehydration reactions; activation energies of dehydrogenation and dehydration coincide for simple catalysts, but vary in the case of mixed catalysts.	Ni and $\text{Al}_2\text{O}_3$ (prepared from metal chlorides, sulfates, or nitrates by precipitation with NaOH or $\text{Na}_2\text{CO}_3$ ).	Balandin and Rubenstein: <i>Zhur. Fiz. Khim.</i> (U.S.S.R.), 6, 576-589 (1935). Zelinsky and Komarewsky: <i>Ber.</i> , 57, 668 (1924). Cremer: (Refer to C. 1933 I 1892).
Dehydrogenation and dehydration of alcohols.	Simple and mixed catalysts.	Motowilowa: <i>Zhur. Khim. Prom.</i> (U.S.S.R.), 12, 1184-1188, 1260-1264 (1935).
Parallel dehydrogenation and dehydration of alcohol; T. 350-530°; in the case of mixed catalyst, $\text{Cr}_2\text{O}_3$ and BeO. C precipitates out; simple catalyst, $\text{Fe}_2\text{O}_3$ and ZnO, a simultaneous pyrolysis of alcohol, as well as its decomposition products with C formation, according to the equation: $2\text{CO} \rightarrow \text{CO} + \text{C}$ , is assumed to cause the precipitation of C; activity of the catalyst not decreased by separation of C.	$\text{Fe}_2\text{O}_3$ , $\text{Cr}_2\text{O}_3$ , ZnO and BeO.	Rubinstein and Gratschewa: <i>Zhur. Fiz. Khim.</i> (U.S.S.R.), 8, 725-735 (1936).
Dehydrogenation and dehydration of: (1) cyclohexanol and methylcyclohexanol to benzene and cyclohexene (0.37%); (2) cyclohexanol to benzene and phenol; (3) cyclohexanol to benzene and phenol (small amount); (4) cyclohexanol to benzene (small amount) and phenol (amount increased); reaction, predominantly dehydrogenation with formation of phenol and cyclohexanone, as well as polymerization of high-boiling unsaturated hydrocarbons.	(1) 41.89% Ni 58.11% Al (the action of Zelinsky and Komarewsky catalyst Cr—Cu in mixture with 60% $\text{Al}(\text{OH})_3$ is similar to Ni—Al catalyst) (2) 97.67% Ni 2.33% Al (3) 54.52% Ni 45.48% Al and 85.2 % Ni 14.8 % Al (4) 89.91% Ni 10.09% Al.	Massina: <i>Zhur. Obshchei Khim.</i> (U.S.S.R.), 7 (69), 2128-2136 (1937). Zelinsky and Komarewsky: <i>Ber.</i> , 57, 668 (1924).

Table 6. Catalytic Dehydrogenation of Butyl Alcohol.

Reaction	Catalyst	Observer
Dehydrogenation of <i>n</i> -butyl alcohol to butyraldehyde; yield, 50% of the theoretical and 70% with respect to the starting alcohol; 10% of the theoretical butylbutyrate formed; a small part of butyraldehyde is subject to aldol condensation; T. 450°.	ZnO (2 mm. grain) (40-42 g. ZnO in a tube of 2 cm.).	Riwkin, Nikitina, Paul and Kulbassowa: <i>Sintet. Kauchuk</i> , 5, No. 7/8, 20-30 (1936).
Dehydrogenation of <i>sec</i> -butyl alcohol to methylethyl ketone; no side reaction; T. 250-290°; high yield of ketone, 70-84.3% in the condensate.	Cu-U.	Iwannikow, Tatarskaja and Gawrilowa: <i>Ibid.</i> , 5, No. 9, 16-18 (1936). Iwannikow, Tatarskaja and Gawrilowa: (Refer to C. 1936 I 4988).

Table 6 (Continued).

Reaction	Catalyst	Observer
Dehydrogenation of <i>n</i> -butyl alcohol and isopropyl carbinol; it is ascertained that the normal alcohol dehydrogenates more readily than its isomer; in the reaction, very little by-products are obtained, indicating slight decomposition of butyraldehyde, as well as methylethyl ketone; the activation energy for <i>n</i> -butyl alcohol at 300–400° is 12–13 k. cal./mol; for isopropyl carbinol, a corresponding value is obtained.	Rhenium (the Re catalyst prepared by the hydrazine method from NaReO <sub>4</sub> is essentially more active than that prepared from NH <sub>4</sub> ReO <sub>4</sub> by H <sub>2</sub> reduction).	Platonow and Anissimow: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>7</b> (69), 1360–1363 (1937).

Table 7. Catalytic Dehydrogenation of Propyl and Isopropyl Alcohol.

Reaction	Catalyst	Observer
Dehydrogenation of isopropyl alcohol to acetone; (industrial process).	ZnS (CdS), Zn <sub>3</sub> P <sub>2</sub> .	Sabatier and Senderens: <i>Compt. rend.</i> , <b>136</b> , 738, 921, 983 (1903). Sabatier and Senderens: <i>Ann. chim.</i> (8), <b>4</b> , 332 (1905). I. G. Farbenindustrie A.-G.: E.P. 262,120 (1926). E.P. 263,877 (1927). U.S.P. 1,684,634 (1926).
Dehydrogenation of isopropyl alcohol to acetone.	Cu + Zn. Ag.	Rössler and Hasslacher Chemical Co.: U.S.P. 1,555,539, Sept. 29, 1925. Holzverkohlung Gesellschaft und Industrie A.-G.: G.P. 422,729 (1923).
Dehydrogenation of isopropyl alcohol and cyclohexanol are equal at 230–270°; it is assumed that molecules of both alcohols adhere to the copper surface with the HOHC group; the ketone originating is adsorbed by the catalyst; surface as strong as the alcohol.	Cu.	Balandin, Maruschkin and Ikonnikov: <i>Wiss. Werke Moskau, Mendelejeff, chem.-tech. Inst.</i> , <b>2</b> , 221–224 (1934).
Dehydrogenation of propyl and isopropyl alcohol to propionaldehyde and acetone; T. 200–450°; Re and Cu give almost the same yields (layers of equal thickness); in the case of isopropyl alcohol, the dehydrogenation velocity is considerably higher, and the acetone yield considerably higher for Re than for Cu.	Re (layer of 2 g. of pure metal) (optimum dehydrogenation temp. for Re, 400°). Cu (optimum dehydrogenation temp. for Cu, 300°).	Platonow, Anissimow and Kraschennikowa: <i>Ber.</i> , <b>69</b> , 1050–1053 (1936).
Dehydrogenation of propyl alcohol.	Re.	Platonow, Anissimow and Kraschennikowa: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>6</b> (68), 855–861 (1936).
Dehydrogenation of alcohols with more than two C atoms, for example, isopropyl alcohol to acetone; T. 400–700°; yield, 71%.	Charcoal, in pieces or finely divided in Fe tube, Cu, brass, Ag, glass, Cr, Cr-Ni, Cr-Mo steels.	Eastman Kodak Co. (McMahon and Kimble): U.S.P. 2,087,038, July 13, 1937.
Dehydrogenation of aliphatic secondary alcohols (isopropyl alcohol, secondary hexyl alcohols) to ketones.	Oxides of Ce, Zn, Mg, Mn, Cr, etc., on a carrier with a heat conductivity of at least 0.2; the catalyst is so prepared that the oxide may be worked out with water to a paste which is coated on filings or small pieces of Cu, Al, brass, steel, or Carborundum.	Standard Alcohol Co.: F.P. 827,467, April 27, 1938.
Dehydrogenation and action of heat on allyl alcohol.	RhO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , MnO <sub>2</sub> , WO <sub>3</sub> .	Sabatier and Kubota: <i>Compt. rend.</i> , <b>173</b> , 17 (1921).
Dehydrogenation of isoamyl alcohol to isoamyl ester and isovaleric acid; T. 280°; yield, 62–65%.	Cu-U.	Abramow and Dolgow: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>7</b> (69), 1009–1014 (1937).

Table 8. Catalytic Dehydrogenation of Cyclic Alcohols.

Reaction	Catalyst	Observer
Dehydrogenation of cyclohexanol to ethers.		Lacourt: <i>Bull. soc. chim.</i> , <b>36</b> , 346-358 (1927).
Simultaneous hydrogenation and dehydrogenation of 2 parts cyclohexanol with one part phenol; T. 200°; a quantitative yield of cyclohexanone obtained.	Hydrogenation catalysts.	Schering-Kahlbaum: Swiss P. 141,528 (1930).
Dehydrogenation of aliphatic or cyclic alcohols to esters.	Cu or Ni precipitated on Al gel.	Dupont: U.S.P. 2,004,350 (1935).
Dehydrogenation of cyclohexanol led to the formation of cyclohexanone beside traces of phenol; because of a weak dehydration process of cyclohexanol, likewise small amounts of hydrocarbons (cyclohexene and benzene are formed); yield 23.2-25.3% of the ketone obtained at 350-400°; at 500° the gas consisted of pure H <sub>2</sub> .	Rhenium (prepared by the HNO <sub>3</sub> method in a finely dispersed state); addition of ReS <sub>2</sub> to the catalyst leads to a strong increase in phenol formation, while cyclohexanol is obtained in a small amount.	Tur, Anissimow and Platonow: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>7</b> (69), 2895-2898 (1937).
Dehydrogenation of sugar alcohols, mannite and dulcitol, to hexose; T. 80-85°; mannite dehydrogenates first to <i>d</i> -mannose and <i>d</i> -fructose; <i>d</i> -mannose changes further into <i>d</i> -mannonic acid, then into <i>d</i> -mannuronic acid and <i>d</i> -mannosaccharinic acid (small amount of keto-mannonic acid formed); <i>d</i> -fructose is dehydrogenated to <i>d</i> , <i>l</i> -galactose, <i>d</i> , <i>l</i> -tagatose, <i>d</i> , <i>l</i> -galactonic acid, <i>d</i> , <i>l</i> -galactoson, 2-keto- <i>d</i> , <i>l</i> -galactonic acid, <i>d</i> , <i>l</i> -galacturonic acid and mucic acid.	Pt; Pt-oxy-monohydrate and O <sub>2</sub> , or better air, passed through under atmospheric pressure.	Glattfeld and Gershon: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 2013-2023 (1938); refer also to Schimpf: Dissertation, University of Chicago (1935).

Table 9. Catalytic Dehydrogenation of Nitro-Compounds.

Reaction	Catalyst	Observer
Dehydrogenation of amino-acids.	Alloxan.	Stecker: <i>Ann.</i> , <b>123</b> , 363 (1862).
Dehydrogenation of amino-acids.	Quinone and isatine.	Traube: <i>Ber.</i> , <b>44</b> , 3145 (1911).
Dehydrogenation of amino-acids.	Isatine and its derivatives.	Langenbeck: <i>Ber.</i> , <b>60</b> , 930-934 (1927).
Dehydrogenation of amino-acids in the presence of methylene blue or O <sub>2</sub> as H <sub>2</sub> acceptors.	Isatine-bromine, isatine-chlorine, <i>n</i> -methyl-isatine and isatine-5-sulfo-acid.	Langenbeck: <i>Ber.</i> , <b>60</b> , 930-934 (1927); <b>61</b> , 942 (1928).
Dehydrogenation of aromatic amines (diphenylamine, aniline) to carbazene (direct conversion).	Pt-charcoal.	Zelinsky, Titz and Gawerdowskaja: <i>Ber.</i> , <b>59</b> , 2590 (1926).
Dehydrogenation of isobutylamine to the nitrile of isobutyric acid, and turpentine to <i>n</i> -cymene.	Mixture of Zn and Cd salts of arsenic acid or ZnPO <sub>3</sub> .	I. G. Farbenindustrie A.-G.: U.S.P. 1,684,634 (1928).
Dehydrogenation of pyridine to 2,2-dipyridyl at 320° and quinoline to 2,2'-diquinoyl at 320-335°.	Ni-Al <sub>2</sub> O <sub>3</sub> (Zelinsky-Komarewsky).	Wibaut and Willink: <i>Rec. trav. chim.</i> , <b>50</b> , 287 (1931); <b>54</b> , 804 (1935).

Table 10. Catalytic Dehydrogenation of Aromatic Hydrocarbons.

Reaction	Catalyst	Observer
Dehydrogenation of hydroquinone.	Neutral salts of aliphatic oxyacids in joint action with an inorganic catalyst, i.e., a neutral or acid solution with Mn salts; Mn salts alone catalyze only the conversion of hydroquinone to quinone.	Euler and Bolin: <i>Z. physiol. Chem.</i> , <b>57</b> , 80 (1908); <b>61</b> , 172 (1909). Euler and Bolin: <i>Z. physik. Chem.</i> , <b>69</b> , 187 (1910). Wieland and Fischer: <i>Ber.</i> , <b>59</b> , 1188 (1926).



Table 10 (Continued).

Reaction	Catalyst	Observer
Dehydrogenation of hexahydrobenzene to benzene; T. 300°.	Ni—Al <sub>2</sub> O <sub>3</sub> catalyst prepared by method of Zelinsky and Komarewsky.	Pfaff and Brunck: <i>Ber.</i> , <b>56</b> , 2463 (1923). Zelinsky and Komarewsky: <i>Ber.</i> , <b>57</b> , 667 (1924).
Dehydrogenation of aromatic hydrocarbons to styrene and its homologs.		Naugatuck Chemical Co.: U.S.P. 1,541,175, June 9, 1925.
Dehydrogenation of organic cpds.: mineral oils, benzene, naphthenes, carbon, hydrogenation products and tar; T. 200–300°; increased or decreased pressure; fractions boiling over 80° led over catalysts.	Catalysts, in addition to Co and Fe, contain also metals of the 5th to 9th groups; V, Mo, W, Nb, Ta, Cr, Mn, or their oxides; Pb, Sn, Zn, Cd and solid oxides of non-metals of the 5th group (P, As, Sb); catalysts are pretreated with H <sub>2</sub> at 200°, also with H <sub>2</sub> S, H <sub>2</sub> Se, KH <sub>3</sub> , CS <sub>2</sub> , HI; e.g., active C is impregnated with ammonium molybdate, Pb(NO <sub>3</sub> ) <sub>2</sub> and H <sub>3</sub> PO <sub>4</sub> and treated at 300° with H <sub>2</sub> S; C impregnated with NH <sub>4</sub> tungstate, Co(NO <sub>3</sub> ) <sub>2</sub> and Sb <sub>2</sub> O <sub>3</sub> and treated with H <sub>2</sub> S at 350°; C impregnated with NH <sub>4</sub> vanadate, Co(NO <sub>3</sub> ) <sub>2</sub> and H <sub>3</sub> PO <sub>4</sub> and heated at 350° with H <sub>2</sub> and CS <sub>2</sub> ; uranium oxide may also be present.	I. G. Farbenindustrie A.-G.: E.P. 333,995, Sept. 18, 1930.
Dehydrogenation of aromatic hydrocarbons containing one C atom aliphatic side chains: triphenyl benzene, as well as some diphenyl benzene, obtained by passing benzene vapor over a catalyst at 500–800°.	Catalysts comprising one or more difficultly reducible but readily fusible metal oxides or cpds. decomposing into oxides deposited on a carrier: a mixture of potash, ThO <sub>2</sub> and Co oxide deposited on pumice.	I. G. Farbenindustrie A.-G.: B.P. 369,613, Dec. 17, 1930.
Dehydrogenation of ethyl benzene, isopropyl benzene, diethyl benzene to styrene in the presence of N <sub>2</sub> ; T. 500–700°; yield, 30%.	Anthracite, active charcoal, silica gel, bauxite, Al <sub>2</sub> O <sub>3</sub> ; active charcoal impregnated with 5% LiOH.	I. G. Farbenindustrie A.-G. (Marx and Wulff): G.P. 550,055 (1931). G.P. 560,686 (1931).
Dehydrogenation (unconfirmed) of hydroquinone; Pd charged with H <sub>2</sub> hydrogenates hydroquinone even when quinone is present; Pd black (Gutbier's method) causes no dehydrogenation of hydroquinone; it is assumed that dehydrogenation with Pd black is successful only when Pd(OH) <sub>2</sub> is present.	Pd black.	Gillespie and Lin: <i>J. Am. Chem. Soc.</i> , <b>53</b> , 3969–3992 (1931).
Dehydrogenation of pressure hydrogenation products in vapor phase; aromatic hydrocarbons obtained.	Catalysts splitting off H <sub>2</sub> ; active charcoal or cpds. of the 6th group, e.g., Mo oxides or ZnO; Al <sub>2</sub> O <sub>3</sub> mixed with CdS, ZnS, or Cr <sub>2</sub> O <sub>3</sub> .	I. G. Farbenindustrie A.-G. (Mittasch, Pier, Wietzel and Langheinrich): U.S.P. 1,913,940 and 1,913,941, June 13, 1933.
Dehydrogenation of benzene from Nowo-Bogatinsk (Emba) crude at 160°; 43% crude oil with high content of aromatic hydrocarbons further aromatized by catalytic dehydrogenation forming benzene, toluene and xylene.	30% Pt, active charcoal or Ni—Al <sub>2</sub> O <sub>3</sub> .	Zelinsky and Schujkin: <i>Khim. Zhur.</i> , <i>Ser. A</i> , <b>4</b> (66), 901–905 (1934).
Dehydrogenation of a Ssurachan benzene fraction rich in hydroaromatics obtained from Baku crude; 70% after first fractionation at 300°; complete dehydrogenation at 300°.	Ni on Al <sub>2</sub> O <sub>3</sub> ; Pt on active charcoal; both catalysts desulfurize benzene.	Zelinsky and Schujkin: <i>Bull. acad. sci. U.R.S.S.</i> , <b>7</b> , 229–237 (1935).
Dehydrogenation of hydroaromatic carboxy-acid derivatives and ketones.	Se.	Ruzicka: <i>Helv. Chim. Acta</i> , <b>19</b> , 419–423 (1936).

Table 10 (Continued).

Reaction	Catalyst	Observer
Dehydrogenation of ethyl benzene to styrene; separation of styrene from unchanged ethyl benzene effected by polymerization in the presence of benzoyl peroxide (0.5%) at 90–100° for 44 hrs. 140–150° for 23 hrs. 180–200° for 13–18 hrs.	Oxides of Mg, Cr, or Zn + Al <sub>2</sub> O <sub>3</sub> .	Salkind and Bulawski: <i>Plasticheskie Massy</i> , 3, 9–12 (1935). Salkind and Bulawski: F.P. 702,397. Salkind: <i>Zhur. Obshchei Khim.</i> (A), 1 (63), 151–62 (1931).
Dehydrogenation of ethyl benzene and other aromatic hydrocarbons containing one or two nuclei and with one aliphatic side chain of at least two C atoms to styrene.	CeO <sub>2</sub> and ZnO, also W, U, Mo and Si oxides.	Dupont (Graves): U.S.P. 2,036,410, April 7, 1936.
Dehydrogenation of narrow benzene-ligroin fractions of Koss Tschagui; dearomatized fractions consisting of poly methylene- and paraffinic hydrocarbons are led in the vapor phase at 310° into a weak H <sub>2</sub> stream over the catalyst; in the products obtained by repeated passage the content of aromatics is determined from the <i>D</i> and <i>n<sub>D</sub></i> values, and after sulfonation the content in naphthenes and paraffins is established from the aniline point; it was ascertained that thereby not only are the hexamethylene hydrocarbons dehydrogenated, but also the paraffinic hydrocarbons, probably of an isostructure, are cyclized and dehydrogenated.	Platinized charcoal (65 g. H <sub>2</sub> PtCl <sub>6</sub> · 6H <sub>2</sub> O on 70 g. activated charcoal); the poisoning of the catalyst by S cpds. is reversible and may be prevented by energetic passage of H <sub>2</sub> at 315–320° in the presence of cyclohexane.	Zelinsky, Mussajew and Halpern: <i>Invest. Akad. Nauk S.S.S.R.</i> , 1937, 467–79.
Dehydrogenation of hydrogen-rich benzenes or single hydrocarbons above 250°, especially 350–500°; high antiknock benzenes, rich in aromatics, are obtained.	Al <sub>2</sub> O <sub>3</sub> + 1–40% metals or compounds of metals of the 6th group of the periodic system.	I. G. Farbenindustrie A.-G.: E.P. 502,961, April 27, 1939.

Table 11. Catalytic Dehydrogenation of Hydronaphthalenes.

Reaction	Catalyst	Observer
Dehydrogenation of decahydronaphthalene to naphthalene; T. 333°.	Pt-charcoal; Pt-asbestos.	Zelinsky and Balandin: <i>Z. physik. Chem.</i> , 126, 267–289 (1926). Zelinsky and Balandin: <i>Ber.</i> , 59, 2580 (1927).
Dehydrogenation of decahydronaphthalene.	Os.	Balandin: <i>Z. physik. Chem.</i> (B), 9, 49–72 (1930).
Dehydrogenation of hydronaphthalene; octalenes are disproportionated at c.p. into Decalin and Tetralin; T. 300°; Decalin is dehydrogenated very slowly at 300°, but above readily; in the presence of angular methyl groups at 200°, no dehydrogenation or disproportionating takes place, but at 300° these cpds. are dehydrogenated and, depending upon the catalyst, the angular methyl group is either split off or migrates toward the $\alpha$ -carbon atom.	Pt, Pd.	Linstead, Millidge, Thomas and Walpole: <i>J. Chem. Soc.</i> , 1937, 1146–1157.
Dehydrogenation of hydroaromatic hydrocarbons to aromatics; benzene with high octane number obtained; in addition to this reaction a ring splitting of the hydroaromatics takes place with formation of low-boiling aromatic hydrocarbons, e.g., with Tetralin a reaction product (yield 86–98%; b.p. 120–215°) is obtained consisting of 90–95% aromatics; paraffinic hydrocarbons subjected to the same conditions are likewise converted partially into aromatics; <i>n</i> -decane (Kahlbaum) gave a reaction product (yield 70%; b.p. 40–179°) consisting of 44.8% aromatics, 8.4% naphthenes, 24.6% unsaturated hydrocarbons and 22.2% paraffinic hydrocarbons.	Activated Cr and Cu oxides.	Karzhev, Severjanova and Sisowa: <i>Oil and Gas J.</i> , 37 (4), 50, 53, (1938).

Table 12. Catalytic Dehydrogenation of Anthracene.

Reaction	Catalyst	Observer
Dehydrogenation of pitch obtained by destructive distillation to anthracene, dimethyl anthracene, Pyrene, chrysene, picene, tetramethyl picene and naphthanthracene; it is concluded that nuclei of polycyclic aromatic cpds. are contained in pitch also.	Mixtures obtained by the reduction of Fe and Mo oxides.	Hügel and Frangopol: <i>Ann. combustibles liquides</i> , <b>7</b> , 225-338, 417-467 (1932).
Dehydrogenation of octahydro- and dihydro-anthracene and acenaphthene (hydrocarbons with condensed rings); in the case of the first two, anthracene is obtained; acenaphthene remains unchanged; T. 300-310°.	20% Pt on activated charcoal.	Titz and Bergo: <i>Uchenye Zapiski Moskov. Gosudarst. Univ.</i> , <b>6</b> , 353-357 (1936).

Table 13. Catalytic Dehydrogenation of Acenaphthene.

Reaction	Catalyst	Observer
Dehydrogenation of acenaphthene to acenaphthylene; T. 500-800°.	Oxides of alkaline earths and oxides of metals of the 2nd to 4th groups of the periodic system, e.g., a mixture of Zn molybdate and MgO, or ZnO + Al <sub>2</sub> O <sub>3</sub> covered with anthracite.	I. G. Farbenindustrie A.-G.: F.P. 762,672, April 16, 1934. E.P. 423,885, March 7, 1935. Swiss P. 170,761, Oct. 1, 1934.

Table 14. Catalytic Dehydrogenation of Indene.

Reaction	Catalyst	Observer
Dehydrogenation of indene to chrysene.	Reducible, non-volatile oxides of the 2nd and 7th groups on silicic acid gel or bleaching earth.	I. G. Farbenindustrie A.-G. (Wulff and Treppenhauer): G.P. 596,191 (1934).
Dehydrogenation of indene homologs, also $\alpha$ - and $\beta$ -methyl hydriene to naphthalene; T. 450°; indene derivatives heated to 350° convert into hydriene derivatives which are hydrogenated at this temp.	Pd-charcoal.	Ruzicka and Peyer: <i>Helv. Chim. Acta</i> , <b>18</b> , 676 (1935).

Table 15. Catalytic Dehydrogenation of Terpenes.

Reaction	Catalyst	Observer
Dehydrogenation of isoborneol to camphor (industrial process).	Cu.	Goldsmith: E.P. 17,573 (1906). Woog: <i>Compt. rend.</i> , <b>145</b> , 124 (1907).
Dehydrogenation of borneol and isoborneol to camphor in the presence of H <sub>2</sub> (industrial process).	Metals which split off H <sub>2</sub> : Ni + 0.14% Na <sub>2</sub> O Ni + 0.5-1.0% NaNO <sub>3</sub> Cu + alkaline earths; charcoal (containing Fe).	Schering: G.P. 217,147 (1908). U.S.P. 1,746,532 (1930). G.P. 219,043 (1908). G.P. 219,044 (1908). G.P. 271,157 (1909).
Dehydrogenation of bicyclic terpenic alcohols, such as borneol, to camphor; T. 350-360°.	Al <sub>2</sub> O <sub>3</sub> .	Ipatieff: <i>Ber.</i> , <b>45</b> , 3205 (1912).
Dehydrogenation of bi- and tricyclic terpene hydrocarbons in the presence of CO <sub>2</sub> ; T. 300°; in addition to dehydrogenation, a splitting of the trimethylene and tetramethylene rings takes place, e.g., carene to cymene.	Platinized charcoal.	Zelinsky and Lewina: <i>Ann.</i> , <b>476</b> , 60 (1929).
Dehydrogenation of terpene hydrocarbons such as pinene or dipinene to cymene: (1) T. 170-185°; yield 25% and 60% polymers; (2) T. 160-220°; good yield of <i>p</i> -cymene; (3) T. 420°; highest yield of cymene.	(1) Fuller's earth or kieselguhr; (2) Al <sub>2</sub> O <sub>3</sub> or active charcoal; (3) Active charcoal.	Hercules Powder Co. (Humphrey): U.S.P. 1,746,532 (1930). U.S.P. 1,893,802 (1933). Bergström, Cederquist and Trobeck: G.P. 625,994 (1936).

Table 15 (Continued).

Reaction	Catalyst	Observer
Dehydrogenation of isoborneol to camphor.	Metal salts, the hydroxides of which are soluble in an excess of $\text{NH}_3$ ; Zn, Cu, Ag, or Cd; $\text{Cu}(\text{NO}_3)_2$ , $\text{Zn}(\text{NO}_3)_2$ , $\text{Cd}(\text{NO}_3)_2$ , $\text{AgNO}_3$ ; carriers: active charcoal, kieselguhr, silica gel, Al gel, or fuller's earth.	Dupont: E.P. 392,134, June 1, 1933.
Dehydrogenation of citral to <i>p</i> -cymene; T. 160–220°; the terpene formed is separated by fractional distillation and reheated with the addition of a catalyst.	Fuller's earth, kieselguhr, $\text{Al}_2\text{O}_3$ and active charcoal are used to split off water from tertiary alcohols.	Bennett and Frazer: U.S.P. 1,893,879, Jan. 10, 1933.
Dehydrogenation of olefinic terpenes to menthene cyclohexene.	Ni.	Sabatier and Gaudion: <i>Compt. rend.</i> , <b>168</b> , 670–672 (1919).
Dehydrogenation of 50 g. piperitone; T. 200–240°; time, 20 hrs.; yield, 13.4 g. phenolic substance containing <i>m</i> -cresol and a small amount of thymol.	25 g. Active charcoal in a cyclic terpene alcohol possesses dehydrogenation ability and the ability to close the ring and polymerize.	Kimura: <i>Bull. Chem. Soc. Japan</i> , <b>10</b> , 330–340 (1935).
Dehydrogenation of terpenes: $\alpha$ -terpineol to dipentene; menthol to menthene; borneol to camphene; geraniol to myrcene; citral to <i>p</i> -cymene; citronellal to isopulegol.		
Dehydrogenation of terpenes.	Charcoal activated by air or water vapor; $\text{NH}_4$ molybdate, sulfide, hydrate, or chloride of Mo on activated charcoal or silicic acid gel.	Bergström, Cederquist and Trobeck: G.P. 625,994 (1936). Swed. P. 85,933 (1935).

Table 16. Catalytic Dehydrogenation of Various Organic Compounds.

Reaction	Catalyst	Observer
Dehydrogenation.	Fe, Co, Cu, $\text{TiO}_2$ , $\text{Li}_2\text{CO}_3$ , or $\text{CaCO}_3$ .	Sabatier: <i>Rev. gen. chim.</i> , <b>17</b> , 221–227 (1912).
Dehydrogenation and hydrogenation.	$\text{NiCO}_3$ , $\text{Ni}(\text{NO}_3)_2$ .	G.P. 282,782, Cl 120, March 16, 1915.
Dehydrogenation.	$\text{Ni}(\text{NO}_3)_2$ .	Dziewonski and Suknarowski: <i>Ber.</i> , <b>51</b> , 457–466 (1917).
Dehydrogenation.	Ti, U, Mn, V, Nb, Ta.	G.P. 207, 989, Kl 120, Sept. 19, 1918.
Dehydrogenation and hydrogenation of oils and fats.	Ni.	Granichstädten and Sittig: <i>Holl. P.</i> 6,568, May 15, 1922.
Dehydrogenation and hydrogenation of C cpds.		Badische Anilin- und Soda Fabrik: G.P. 362,143, Kl 120, Gr 27, Oct. 23, 1922.
Dehydrogenation; kinetics of dehydrogenation catalysis.	Ni, Pt and Pd; Pd, less than Ni and less than Pt.	Zelinsky and Pawlow: <i>Ber.</i> , <b>56</b> , 1249–1255 (1923).
Dehydrogenation and hydrogenation.	Salts of O acids: P, Mo, W, Se and Li, because they are salt-forming bases of alkaline earths.	Badische Anilin- und Soda Fabrik: G.P. 391,673, Kl 120, Gr 27 March 10, 1924.
Dehydrogenation.	Noble metals as dehydrogenation and hydrogenation catalysts.	Zelinsky and Turowa-Pollak: <i>Ber.</i> , <b>58</b> , 1298–1303 (1925).
Dehydrogenation and hydrogenation of organic cpds.	Alloys: Cu-Mg, Ni-Mg	Badische Anilin- und Soda Fabrik: G.P. 408,811, Kl 120, Gr 27, Jan. 24, 1925.
Dehydrogenation and hydrogenation.	Metal oxides.	Sabatier and Fernandez: <i>Compt. rend.</i> , <b>185</b> , 241–247 (1927).
Dehydrogenation.	$\text{ZnS}$ or $\text{CdS}$ on pumice.	I. G. Farbenindustrie A.-G.: E.P. 262,120, Jan. 26, 1927.
Dehydrogenation.	Phosphides, selenides, tellurides, antimonides, arsenides, or bismutites of heavy metals, particularly Zn, are used as catalysts for dehydrogenation.	I. G. Farbenindustrie A.-G.: E.P. 263,897, March 2, 1927; add to G.P. 262,120, May 19 (1927).

Table 16 (Continued).

Reaction	Catalyst	Observer
Dehydrogenation catalysis.	Cu; Cu(OH) <sub>2</sub> precipitated from an alkaline copper salt solution; suspension heated in the mother liquor gradually up to, but under the critical point until $n_{CuO \cdot H_2O}$ is formed ( $n$ =greater than 1); the addition of a suitable dehydrogenation stabilizer, Ca(OH) <sub>2</sub> , Ba(OH) <sub>2</sub> , or Na <sub>2</sub> SO <sub>4</sub> , prevents the further splitting off of water.	Société des Produits Chimiques: P.P. 660,450 (1929).
Dehydrogenation catalysis.	Alumina, as a catalyst, applicable in commercial dehydrogenation processes; kaolin, to which 30% Al <sub>2</sub> O <sub>3</sub> has been added, is suitable to a limited extent as a dehydrogenation catalyst; best catalysts obtained by the precipitation of Al(OH) <sub>3</sub> from Na aluminate with HCl, or from Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> with ammonia, using Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ; large quantity mercaptans formed by the catalytic decomposition of alcohol.	Alexejewski and Prejis: <i>Zhur. Priklad. Khim. (U.S.S.R.)</i> , <b>3</b> , 859-862 (1930).
Dehydrogenation of organic compounds.		Selden Co. (Jaeger): U.S.P. 1,827,317, Oct. 13, 1931.
Dehydrogenation catalysis.	Pumice or coke impregnated with a conc. solution of metal salt mixtures Cu, Cr, or Mg which have the property of splitting off their volatile acids at high temp. without poisoning the catalyst; the salts are converted into their oxides by heating to 500°.	Howard & Sons, Ltd. (Blagden and Clark): E.P. 363,776, Jan. 21, 1932.
Dehydrogenation of butyl mercaptan to thiophene; T. 650-700°.	Silicic acid gel.	Maible and Renaudie: <i>Compt. rend.</i> , <b>195</b> , 391 (1932).
Dehydrogenation and hydrogenation of organic compounds; <i>p</i> -cyclohexyl dehydrates to <i>p</i> -phenylphenol at 295-300°.	Metal catalysts such as Pd electrolytically precipitated from a Pd chloride solution upon a metal in which the Pd is precipitated cathodically in dilute H <sub>2</sub> SO <sub>4</sub> ; ppt. heated at 300-400° in an O <sub>2</sub> stream after which temp. is reduced to between 200-400°, <i>e.g.</i> , the Pd wire gauze is covered with Pd in the prescribed manner.	Dow Chemical Co. (Bass): U.S.P. 1,907,710, May 9, 1933.
Dehydrogenation of ethyl succinate to ethyl fumarate.	SeO <sub>2</sub> .	Austin, Newman and Riley: <i>Ann. Rep. Progress Chem.</i> , <b>391</b> (1933).
Dehydrogenation of organic cpds.	Halogen cpds. of Cu, Ag, Zn, Cd, Pb, Sn, Ti, Si, V, Bi, Mo, W, U, Mn, Re, Ni, Fe or Co; carriers are active C or active SiO <sub>2</sub> .	I. G. Farbenindustrie A.-G.: P.P. 748,442, July 4, 1933.
Dehydrogenation of acetylacetone to diacetylene.		Armstrong and Robinson:
Dehydrogenation of acetone to methylglyoxal.	SeO <sub>2</sub> .	Riley, Morley and Friend: <i>J. Phys. Chem.</i> , <b>36</b> , 1875 (1932).
Dehydrogenation of olefins to diolefins: pseudobutylene to butadiene; T. 300-700°; yield, 25-29%.	Anthracite or silicic acid gel.	Fedorow, Smirnow and Seemenow: <i>Zhur. Priklad. Khim. (U.S.S.R.)</i> , <b>7</b> , 1166 (1934).
Dehydrogenation catalysis.	Ni or Cu or their alloys in the form of wire or filings; Ni, subjected to anodic oxidation in an electrolytic cell; current density below a value of 0.05 amp./sq.in. (about 0.008 amp./sq.cm.).	Technical Research Works, Ltd.: Austrian P. 17,712, Jan. 3, 1935.

Table 16 (Continued).

Reaction	Catalyst	Observer
Dehydrogenation of hydrogenated $\alpha$ -pyridone (hydroxypyridine) derivatives to pure aromatic cpds. not hydrogenated; T. 200–270°; reaction same for their quinoline and isoquinoline derivatives; similarly, carbostyryl (2-hydroxy-quinoline) takes up 2 H atoms and by retaining the O atom is converted into dihydrocarbostyryl; <i>n</i> -methyl- $\alpha$ -pyridine, subjected to conditions under which aromatic rings are not attacked, is readily hydrogenated to <i>n</i> -methyl- $\alpha$ -piperidone; <i>n</i> -methyl-iso-carbostyryl is hydrogenated to a dihydro- derivative; hydrocarbostyryl and hydro-iso-carbostyryl give better yields than the piperidone.	Pt black.	Spáth and Galinovsky: <i>Ber.</i> , <b>69</b> , 2059–2061 (1936).
Dehydrogenation of pyrroline to a mixture of pyrrole and pyrrolidine.	Pt (an 8 cm. layer of Pt asbestos).	Wibaut and Proost: <i>Rec. trav. chim.</i> , <b>52</b> , 333–336 (1933). Hackman: <i>Chem. Abs.</i> , <b>27</b> , 511 (1933). <i>Rec. trav. Chim.</i> , <b>51</b> , 1157–1165 (1932).
Dehydrogenation of dihydronicotyrin to a mixture of dinicotine and nicotyrin; catalytic disproportionation investigated than that of pyrrolidine; in the gaseous phase the reaction takes place at 220°; presence of pyrrole, as well as pyrrolidine, in the distillate was proved by picrates; in Ac(OH) the presence of pyrrole was proved, but not that of pyrrolidine; boiling 4 g. pyrroline for 8 hrs., the presence of both disproportionation products were again shown; pyrrole in the presence of pyrroline and/or pyrrolidine is detected by the formation of pyrrole blue with isatine and the reaction with phenanthrene quinone.	Pt (an 8 cm. layer of Pt asbestos).	Wibaut and Proost: <i>Rec. trav. chim.</i> , <b>52</b> , 333–336 (1933).
Dehydrogenation of one mol furan and 3 mols aniline to <i>n</i> -phenyl pyrrol; theoretical yield, 24%; with <i>o</i> -toluidine, <i>o</i> -tolylpyrrol forms; T. 465°; theoretical yield, 40.6%.	Al <sub>2</sub> O <sub>3</sub> .	Jurjew: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>7</b> (69), 267–269 (1977).
Dehydrogenation and cyclization of hydrocarbons of the paraffin series, e.g., dehydrogenation of cyclohexane and cyclization of <i>n</i> -octane.	Glass, silica gel, ZnO, TiO <sub>2</sub> , MoO <sub>3</sub> , MoS <sub>2</sub> ; glass and silica gel found inactive.	Moldawski, Kamuscher and Kobylskaja: <i>Ibid.</i> , <b>7</b> (69), 1835–1839 (1937).
Dehydrogenation of cyclohexane; T. 510°; yield, 9% benzene and 2% unsaturated hydrocarbons; rate, 6.0 cc./hr.	ZnO (40 cc.).	
Cyclization of <i>n</i> -octane; T. 513°; yield, 4% aromatics and 6.7% unsaturated hydrocarbons; rate, 6.5 cc./hr.		
Dehydrogenation of cyclohexane; T. 500°; yield, 43% benzene; rate, 7.5 cc./hr.	TiO <sub>2</sub> (40 cc.).	
Cyclization of <i>n</i> -octane; T. 510°; yield, 27% aromatics and 2.7% unsaturated hydrocarbons; rate, 7.5 cc./hr.		
Dehydrogenation of cyclohexane; T. 425°; yield, 28% benzene; rate, 8.5 cc./hr.	MoO <sub>3</sub> (30 cc.) on coa.	
Cyclization of <i>n</i> -octane; T. 430°; yield, 33% aromatic and unsaturated hydrocarbons; rate, 5.5 cc./hr.		
Dehydrogenation of cyclohexane; T. 380°; yield, 22% benzene and 0.5% unsaturated hydrocarbons; rate, 6.0 cc./hr.	MoS <sub>2</sub> (40 cc.).	
Cyclization of <i>n</i> -octane; T. 380°; yield, 2% aromatics and 4.1% unsaturated hydrocarbons; rate, 6.0 cc./hr.		
Dehydrogenation of cyclohexane; T. 450°; yield, 35% aromatics and 6% unsaturated hydrocarbons.	MoS <sub>2</sub> (19 cc.).	
Dehydrogenation and cyclization of hydrocarbons, e.g., dehydrogenation of cyclohexane and cyclization of <i>n</i> -octane and diisobutyl; T. 500–550°.	Over various charcoals: charcoal and coal obtained by pyrolysis of benzene over Fe filings at 600°; both kinds are suitable; deactivation of the catalyst by precipitation of high molecular H-poor substances is repressed by high temp. leading to a further splitting off of H <sub>2</sub> and formation of catalytic acting new C surfaces.	Moldawski, Besproswannaja, Kamuscher and Kobylskaja: <i>Ibid.</i> , <b>7</b> (69), 1840–1847 (1937).

Table 16 (Continued).

Reaction	Catalyst	Observer
Dehydrogenation, as well as polymerization of hydrocarbons.	Acid or basic cpds. such as $\text{MgO}$ and $\text{Al}_2\text{O}_3$ ; $\text{MgO}$ and $\text{NaF}$ heated to $870^\circ$ ; with catalytically acting substances, such as acid cpds.; silicates may be used also; acids of metals of the 6th group; oxides of Bi, Sn, Pb, Sb, Co, As, V, P, B; these catalysts are hard and stable.	Standard Oil Development Co. (Sweeney and Spicer): U.S.P. 2,112,387, March 29, 1938.
Dehydrogenation-polymerization of ethylene with $\text{H}_3\text{PO}_4$ ; T. $300^\circ$ and $350^\circ$ ; yield, 21.9–57.0% aromatics for fractions c.p. $150\text{--}180^\circ$ and $180\text{--}225^\circ$ ; with thermal polymerization without $\text{H}_3\text{PO}_4$ ; T. $300^\circ$ ; yield, 33% aromatics; (polymerization of olefins proceeds according to Ipatieff and Pines in several steps: (1) polymerization of olefins; (2) cyclization of olefins to naphthenes; (3) dehydrogenation of naphthenes to aromatics, and (4) hydrogenation of polymer olefins to paraffins.	Ni.	Komarewsky and Balai: <i>Ind. Eng. Chem.</i> , <b>30</b> , 1051–1053 (1938); Ipatieff and Pines: (Refer to C. 1936 I 2057). <i>Ind. Eng. Chem.</i> <b>27</b> , 1364–69 (1935).
Dehydrogenation and cracking of heavy benzine in a cracking chamber after treatment in a heated spiral at about $510^\circ$ and 56 atm. without a catalyst; the cracking tar formed is separated and the vapors are treated in a second zone at one atm. and $535^\circ$ over catalysts; if necessary the vapors, before entering the 2nd zone, are washed with a solvent such as tricresyl phosphate, or led over fuller's earth.	Fuller's earth or other dehydrogenation catalysts such as $\text{ZnO}$ and $\text{Cr}_2\text{O}_3$ on $\text{Al}_2\text{O}_3$ .	Standard Oil Development Co. (Fulton): U.S.P. 2,125,714, Aug. 2, 1938.
Dehydrogenation and cyclization of $\pi$ -heptane at $475^\circ$ to form toluene and heptene; there is no evidence of formation of cyclopentadienes, cycloolefins, di- or triolefins; however, the possibility of intermediary formation of the first two groups is not excluded; the toluene conc. steadily increases with the duration of the reaction, while the heptene conc. remains constant after a definite time; a kind of an equilibrium: paraffin $\rightleftharpoons$ olefin + $\text{H}_2$ or the stationary state, in which the heptene is removed as quickly as it is formed, has been assumed; the fact that the ratio $[\text{C}_7\text{H}_{14}]/[\text{C}_7\text{H}_{12}]$ remains constant favors the second assumption; the results are in agreement with thermodynamics.	Dehydrogenation catalyst.	Pitkethly and Steiner: <i>Trans. Faraday Soc.</i> , <b>35</b> , 979–984 (1939).

## PART XIII

## CATALYTIC HALOGENATION

## Catalytic Chlorination in Inorganic Chemistry

Table 1. Preparation of Chlorine.

Reaction	Catalyst	Observer
Deacon-Hurter process: $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{Cl}_2 + 2\text{H}_2\text{O}$ T. $450\text{--}500^\circ$ ; (industrial process).	Small pieces of broken brick impregnated with $\text{CuCl}$ ; Cu content of catalyst, 0.6–0.7%.	Deacon: <i>J. Chem. Soc.</i> , <b>25</b> , 725, (1872). Deacon: <i>Brit. Assoc. Advancement Sci. Rep.</i> , <b>54</b> (1870). Hurter: <i>J. Soc. Chem. Ind.</i> , <b>2</b> , 103 (1883).
Deacon-Hurter process: $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{Cl}_2 + 2\text{H}_2\text{O}$ (1) $\text{Cu}_2\text{Cl}_2 + \text{O}_2 \rightarrow \text{CuO} \cdot \text{CuCl}_2$ (2) $\text{CuO} \cdot \text{CuCl}_2 + 2\text{HCl} \rightarrow 2\text{CuCl}_2 + \text{H}_2\text{O}$ (3) $2\text{CuCl}_2 \rightarrow \text{Cu}_2\text{Cl}_2 + \text{Cl}_2$	Purified dry $\text{HCl}$ .	Hasenclever: <i>Ber.</i> , <b>9</b> , 1070 (1876).
Weldon-Péchiney Process: $2\text{MgCl}_2 + \text{H}_2\text{O} + \text{O} \rightarrow 2\text{MgO} + 2\text{HCl} + \text{Cl}_2$ ; T. $1000^\circ$ .	A solution of $\text{MgCl}_2$ with powdered $\text{MgO}$ in proportions to give $\text{MgO} \cdot \text{MgCl}_2$ ; the solid oxychloride is powdered, dried at $300^\circ$ and passed into brick furnaces in contact with hot air.	Dewar: <i>J. Soc. Chem. Ind.</i> , <b>6</b> , 775 (1887). Moldenhauer: <i>Z. anorg. allgem. Chem.</i> , <b>51</b> , 369 (1906).

Table 1 (Continued).

Reaction	Catalyst	Observer
Weldon process:	Oxide of Mn in varying oxidation stages.	Weldon: E.P. 4,079 (1883). E.P. 5,868 (1883). E.P. 9,307 (1884).
(1) $\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$		
(2) $\text{MnCl}_2 + \text{Ca(OH)}_2 \rightarrow \text{Mn(OH)}_2 + \text{CaCl}_2$		
(3) $2\text{Mn(OH)}_2 + \text{O}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaO} + 2\text{MnO}_2 + 3\text{H}_2\text{O}$		
(4) $2\text{CaO} \cdot 2\text{MnO}_2 + 2\text{Ca(OH)}_2 + \text{MnCl}_2 + \text{O}_2 \rightarrow 2(\text{CaO} \cdot 2\text{MnO}_2) + 2\text{CaCl}_2 + 2\text{H}_2\text{O}$		
(5) $\text{CaO} + 2\text{MnO}_2 + 2\text{HCl} \rightarrow 2\text{MnO}_2 + \text{CaCl}_2 + \text{H}_2\text{O}$		
Production of HCl for chlorination purposes:	Granular activated charcoal.	Paterno: <i>Gazz. chim. ital.</i> , <b>8</b> , 233 (1878). Boshovski and Danilitschenko: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>59</b> , 851 (1927).
(1) from products of the manufacture of caustic soda by electrolysis of brine, <i>i.e.</i> , from H and Cl;		
(2) safe and technically efficient method: equimolecular mixture of $\text{H}_2$ and $\text{Cl}_2$ passed through the catalyst.		

Table 2. Catalytic Chlorination in Inorganic Chemistry.

Reaction	Catalyst	Observer
Chlorination of $\text{SO}_2$ or $\text{H}_2$ in the cold.	C saturated with Cl.	Melseurs: <i>Compt. rend.</i> , <b>76</b> , 92 (1873).
Chlorination reaction.	Catalyst obtained by calcining blood with $\text{K}_2\text{CO}_3$ .	Damoiseau: <i>Ibid.</i> , <b>83</b> , 60 (1876).
Chlorination reaction: $\text{H}_2 + \text{Cl}_2 \rightarrow \text{HCl}$ .	Active charcoal.	James: E.P. 1,831 (1900). Paterno: <i>Gazz. chim. ital.</i> , <b>8</b> , 233 (1878).
Chlorination reaction: addition of $\text{Cl}_2$ in nitrogen adsorption by $\text{CaC}_2$ .		Polszenius: (1901).
Chlorination reaction: $\text{SO}_2 + \text{Cl}_2 \rightarrow \text{SOCl}_2$ (industrial process).	Active charcoal, graphite.	Pope: E.P. 122,516 (1918). Farbenfabrik vorm. Meister Lucius Bruning: G.P.; add to F.P. 55242 (1934). McKee and Salls: <i>Ind. Eng. Chem.</i> , <b>16</b> , 251 (1924). Danneel: <i>Z. angew. Chem.</i> , 1553 (1926).
Chlorination reaction: $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$ $\text{CO} + \text{HCl}$ in the presence of $\text{CuCl}$ behaves as $\text{HCOCl}$ .	Active charcoal.	Askenasy and Mugdan: G.P. 154,657 (1903). (Refer to C. 1898 II 951).

## Catalytic Chlorination in Organic Chemistry

Table 1. Catalytic Chlorination of Paraffinic Hydrocarbons.

Reaction	Catalyst	Observer
Chlorination of $\text{CH}_4$ to $\text{CHCl}_3$ .	Rhenium.	F.P. 68,244.
Chlorination of $\text{CH}_4$ .		Huff: <i>Trans. Am. Electroch. Soc.</i> , <b>36</b> , 167-186 (1920).
Chlorination of $\text{CH}_4$ : $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$ 10 vol. $\text{CH}_4$ , 1 vol. $\text{Cl}_2$ * T. 400°; time, 10 min. 5 vol. $\text{CH}_4$ , 1 vol. $\text{Cl}_2$ ** T. 370°.	Bone charcoal.	Lacy: Austrian P. 88,549 (1922)* C. 1923 II 806. Austrian P. 88,668 (1922).**
Chlorination of $\text{CH}_4$ to $\text{CHCl}_3$ in the presence of $\text{HCl}$ ; at room temp., substitution products of methane obtained.	Dry charcoal.	Carbide and Carbon Chemicals Corporation (Curme): U.S.P. 1,422,838 (1922). Beall: <i>Refiner Natural Gasoline Mfr.</i> , <b>15</b> , 264 (1936).
Chlorination of $\text{CH}_4$ at 300-650° (oxidation of $\text{CH}_4$ avoided by using high streaming velocity). $2\text{CH}_4 + \text{Cl}_2 + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CH}_3\text{Cl} + \text{H}_2\text{O}$ .	Bone or active charcoal.	Holzverkohlungs Industrie A.-G. (Krause and Roxa): U.S.P. 1,591,984 (1926). G.P. 478,083 (1929). Gremli: Austrian P. 108,424 (1928).



Table 1 (Continued).

Reaction	Catalyst	Observer
Chlorination of $\text{CH}_4$ in the presence of $\text{Cl}_2$ and $\text{HCl}$ ; T. $450^\circ$ ; yield, 89% $\text{CH}_3\text{Cl}$ (18 g. $\text{CH}_3\text{Cl}$ obtained from 32 l. $\text{CH}_4$ ).	Pumice impregnated with $\text{CuCl}_2$ + 1% $\text{CeCl}_3$ subjected to 4 hrs. treatment with $\text{N}_2$ at $150^\circ$ .	Giordani: <i>Ann. chim. applicata</i> , 25, 163-173 (1935).
Chlorination of $\text{CH}_4$ to $\text{CCl}_4$ ; yield, 90%.	Active charcoal.	Kiprianow and Kursner: <i>Zhur. Priklad. Khim. (U.S.S.R.)</i> , 8, 673-684 (1935).
Chlorination of $\text{CH}_4$ to $\text{CCl}_4$ , $\text{CHCl}_3$ , $\text{CH}_2\text{Cl}_2$ , $\text{CH}_3\text{Cl}$ , $\text{C}_2\text{H}_5\text{Cl}$ .	A thin, porous layer, or a very fine mesh of resistant material.	I. G. Farbenindustrie A.-G.: F.P. 816,957, Aug. 21, 1937.
Chlorination of $\text{CH}_4$ to $\text{CH}_3\text{Cl}$ , $\text{CH}_2\text{Cl}_2$ in liquid phase.	Action of rays.	I. G. Farbenindustrie A.-G.: F.P. 816,990, Aug. 21, 1937.
Chlorination of $\text{C}_2\text{H}_6$ to 1,1,1-trichlorethane; T. $100-300^\circ$ .	Active charcoal and silicic acid gel.	I. G. Farbenindustrie A.-G. (Müller-Cunradi): G.P. 436,999 (1926).
Chlorination of $\text{C}_2\text{H}_6$ to hexachlorethane.	Active charcoal.	Mamedalijew and Efendijewa: <i>Azerbaidzhanskoe Nefiyanoe Khim.</i> , 16 (7), 66 (1936).
Chlorination of $\text{C}_2\text{H}_5\text{Cl}$ , either thermally, or by treating the monochlorides with $\text{Cl}_2$ over catalyst; T. $170^\circ\text{C}$ .; direct hydrolysis by water of secondary and tertiary chlorides; metathesis with primary and secondary amyl chlorides to amyl oleates readily saponified; amyl alcohols to acetates, sold as high-boiling solvents for nitrocellulose lacquers.	Na oleate and aqueous caustic soda solution.	Sharples Solvents Corporation (Wyandotte); Brooks, Essex and Smith: U.S.P. 1,191,916, July 18, 1918. Koch and Burrell: <i>Ind. Eng. Chem.</i> , 19, 442 (1927). Koch and Stallkamp: U.S.P. 1,380,067, 1932.
Chlorination of $\text{C}_2\text{H}_{12}$ in liquid phase $\text{C}_2\text{H}_{12} + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_{11}\text{Cl} + \text{HCl}$	Active charcoal or silica gel.	Koch and Burrell: <i>Ind. Eng. Chem.</i> , 19, 442 (1927).
Chlorination of $\text{C}_2\text{H}_{12}$ (pentane previously saturated with dry $\text{HCl}$ ; lower layer of $\text{HCl}$ separated by gravity and drained off).		Ayres: <i>Ind. Eng. Chem.</i> , 21, 899 (1929). Ayres: U.S.P. 1,717,136. U.S.P. 1,741,393. U.S.P. 1,835,202, Dec. 8, 1931.
Chlorination of $\text{C}_2\text{H}_{12}$ ; a homogeneous reaction.	Carbonaceous deposit on wall of reaction chamber.	Yuster and Reyerson: <i>J. Phys. Chem.</i> , 39, 859-875 (1935); 39, 1111-1123 (1935).
Chlorination of $\text{C}_2\text{H}_{12}$ ; (the chlorination velocity decreases rapidly with increasing pressure; chain mechanism applied to interpret chlorination reaction).		Hass, McBee and Hatch: <i>Ind. Eng. Chem.</i> , 29, 1335-1338 (1937).
Chlorination reaction influence of $\text{Cl}_2$ and $\text{SO}_2$ upon hydrocarbons.		Horn and Reed: (Refer to C. 1937 I 720). U.S.P. 2,046,090, June 30 (1936).
Chlorination of isobutane to isobutyl chloride which, when separated from the tertiary isomer, is rearranged to tertiary butyl chloride; a mixture of tertiary butyl chlorides is used in the synthesis of <i>tert</i> -butyl phenol for the production of <i>tert</i> -butyl phenol-formaldehyde resins; 1,2-dichlorisobutane containing 1,1-isomer is obtained as a by-product and marketed.		Dow Chemical Co.: U.S.P. 1,800,295 (1931). U.S.P. 1,800,296 (1931). B.P. 334,572 (1930). F.P. 592,548 (1935). G.P. 440,003 (1927). G.P. 548,656 (1932).
Chlorination of 632 g. butene-butylene with cooling by water in the presence of 385 g. $\text{Cl}_2$ to 590 g. butylene chloride; temp. less than $70^\circ$ ; this product is led at the rate of 250 g./hr. at $625^\circ$ under 20 mm. Hg over the catalyst, resulting in the formation of 95% butadiene; butadiene is led over Na lime at $350^\circ$ and washed with $\text{NH}_4\text{Cu}$ salt solution to free it from acetylene hydrocarbons.	100 cc. silica gel.	I. G. Farbenindustrie A.-G.: E.P. 481,612, April 14, 1938.

Table 1 (Continued).

Reaction	Catalyst	Observer
Chlorination of paraffin wax for fire-proofing insulating materials.		Ellis: U.S.P. 1,246,810 (1917).
Chlorination of paraffin wax to serve as a solvent for dichloramine.		Dakin and Dunham: <i>Brit. Med. J.</i> , 1, 51 (1918).
Chlorination by heat of molten paraffin followed by Friedel-Crafts condensation of monochlorides with naphthalene to form "Parafflow"; 1% Parafflow is added to a high pour test lubricating stock which serves to lower the pour point by 35°F.		Deanesly: <i>J. Am. Chem. Soc.</i> , 56, 2501 (1934). Deanesly: B.P. 399,991 (1933).
Chlorination of higher petroleum fractions followed by removal of HCl and formation of double bonds leading to the production of drying oils.		Gardner and Bielouss: <i>Ind. Eng. Chem.</i> , 14, 619 (1922). Refer also to U.S.P. 1,386,447 (1921). U.S.P. 1,412,399 (1922).
Chlorination of 1-chlorobutane by Cl <sub>2</sub> gas to prepare dichlorobutane; four possible isomers are formed: 1,1-dichlorobutane ~ 3% 1,2-dichlorobutane ~ 17% 1,3-dichlorobutane ~ 50% 1,4-dichlorobutane ~ 25%	SbCl <sub>5</sub> .	Tischtschenko and Tschurbakow: <i>Zhur. Obshchei Khim.</i> (U.S.S.R.), 7, (69), 893-896 (1937).
Chlorination of hydrocarbons with not more than 4 C atoms and not more than 3 C atoms in the straight chain; they are converted into 1-chloroparaffin and further with Cl <sub>2</sub> at -65° into 1,3-dichlorides up to the critical temp. of the hydrocarbon; especially suitable is the method for preparation of 1,3-dichlor-2-methylpropane, which is obtained from 1-chlor-2-methylpropane dissolved in an inert solvent above the critical temp.		Purdue Research Foundation (Hass and McBee): Can. P. 378,829, Jan. 10, 1939.
Chlorination of ethane; C <sub>2</sub> H <sub>6</sub> is treated with Cl <sub>2</sub> in gaseous phase in ratio 1 : 2.4 up to 3.5 at 250° or higher; if the reaction is carried out at 400°, the reaction product consists of 45.9% ethyl chloride, 2.9% vinyl chloride, and 3.7% methyl chloride.	Melts of metal chlorides, such as 17.7 parts AlCl <sub>3</sub> , 6.4 parts NaCl and 1.0 part CuCl <sub>2</sub> .	Dow Chemical Co. (Reilly): U.S.P. 2,140,547, Dec. 20, 1938.

Table 2. Catalytic Chlorination of Olefinic Hydrocarbons (Ethylene).

Reaction	Catalyst	Observer
Chlorination of C <sub>2</sub> H <sub>4</sub> in the presence of HCl to ethyl chloride.	Diatomite.	Farbenfabriken vorm. Friederich Bayer and Co. (Liebmann): G.P. 361,041 (1923). E.P. 177,362 (1922). F.P. 532,735 (1923).
Chlorination of C <sub>2</sub> H <sub>4</sub> ; T. 100-200°; pressure, 25-30 atm.	Porous charcoal, e.g., charcoal charged with HCl.	Chemische Fabrik Weiler-ter-Meer (Snida): G.P. 369,702 (1923).
Chlorination and bromination of C <sub>2</sub> H <sub>4</sub> and C <sub>2</sub> H <sub>2</sub> .		Wibaut, Dickmann and Rutgers: <i>Koninkl. Akad. Wetenschappen Amsterdam</i> , 33, 481-495 (1924).
Chlorination of C <sub>2</sub> H <sub>4</sub> to ethyl chloride.	AlCl <sub>3</sub> , MgCl <sub>2</sub> , ZnCl <sub>2</sub> , FeCl <sub>3</sub> , or double cpds., such as AlCl <sub>3</sub> · FeCl <sub>3</sub> (regenerated with Cl <sub>2</sub> at 100°).	Chemische Fabrik Weiler-ter-Meer: E.P. 235,521, July 9, 1925. Austrian P. 106,039, March 25, 1927.
Chlorination of C <sub>2</sub> H <sub>4</sub> to dichloroethylene; T. 120-125° C <sub>2</sub> H <sub>4</sub> + 2Cl <sub>2</sub> → C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> + 2HCl	Active charcoal.	Alexejewski: <i>J. Russ. Phys.-Chem. Soc.</i> , 55, 403 (1925).

Table 2 (Continued).

Reaction	Catalyst	Observer
Chlorination of $C_2H_4$ to hexachlorethane; T. 300–350°; yield, 90% $C_2H_4 + 5Cl_2 \rightarrow C_2Cl_6 + 4HCl$	Active charcoal.	Miller: <i>Ind. Eng. Chem.</i> , <b>17</b> , 1182 (1925).
Chlorination of $C_2H_4$ to 1,2-dichlorethane.	Active charcoal.	Badische Anilin- und Soda Fabrik (Wietzel and Dirksen): G.P. 420,500 (1925).
Chlorination of $C_2H_4$ to dichlorethane.	Charcoal impregnated with $SbCl_3$ .	I. G. Farbenindustrie A.-G. (Engelhardt): G.P. 442,342 (1927).
Chlorination of $C_2H_4$ to 1,2-dichlorethane.	Dehydrated bauxite.	Rhenania-Kunheim Verein Chemische Fabriken A.-G.: G.P. 443,020, Kl 12g, April 19, 1927.
Chlorination of $C_2H_4$ to ethyl chloride: $C_2H_4 + HCl \rightarrow C_2H_5Cl$ (industrial process).	$BiCl_3$ on asbestos; $Fe + FeCl_3$ ; $AlCl_3$ .	Wibaut: G.P. 445,981 (1927). Chemische Fabrik vorm. Fahlberg (List and Co.): G.P. 219,242 (1907).
Chlorination of $C_2H_4$ ; surface reactions between ethylene and the halides.		Mooney and Reid: <i>J. Chem. Soc.</i> , 1931, 2597–2605.
Chlorination of $C_2H_4$ in the preparation of alkyl chlorides; T. 180–220°.	Charcoal or bone charcoal impregnated with 10% $H_3PO_4$ .	Dr. A. Wacker Gesellschaft für Elektrische Industrie (Ernst): G.P. 541,566 (1931). G.P. 583,497 (1933).
Chlorination of $C_2H_4$ in the preparation of alkyl chlorides; T. 200–325°.	$Al(OH)_3$ .	Dupont (Daudt): U.S.P. 1,920,246 (1933).
Chlorination of perchlorethylene to hexachlorethane; T. 80–100°; when combined with distillation, temp. below 120°.	$I_2$ , $AlCl_3$ , $FeCl_3$ , $SbCl_3$ , $SbCl_5$ .	Dupont (Levine and Bond): U.S.P. 2,037,419, April 14, 1936.
Chlorination of $C_2H_4O$ in the presence of $HCl$ with splitting of the ring to form a halogen hydrine.	Kieselguhr or silica gel charged with a heavy metal and $HCl$ , e.g., ferric salt and $HCl$ .	Drägerwerk and Dräger: G.P. 631,178 (1936).
Chlorination of $C_2H_4$ in the presence of $HCl$ ; T. 250°; yield, 62%; at 210° no conversion observed; at 300° dissociation of chlorethane takes place.	$BaCl_2$ .	Balandin and Liwanowa: <i>Nauch. Izvestija Moscow, Gosud. Univ.</i> , <b>2</b> , 237–239 (1934).
Chlorination of $C_2H_4$ to dichlorethane.	Complex cyanide cpds., such as alkali or alkaline earths, ferrocyanide in mixture with one or more metal chlorides, such as $AlCl_3$ or $FeCl_3$ .	N. V. de Bataafsche Petroleum Mij: E.P. 446,411 (1936).
Chlorination of $C_2H_4$ to ethyl chloride.	$Zn$ halide activated by mono- and polyvalent metals precipitated on charcoal, kieselguhr, or silicic acid gel.	I. G. Farbenindustrie A.-G.: E.P. 448,269 (1936).
Chlorination of $C_3H_4$ , $C_4H_{10}$ , vinyl chloride and chlorbutane to $C_3H_7Cl$ ; T. 200°; $C_3H_7Cl_2$ and $C_2H_5Cl_2$ to $C_3H_8Cl$ ; T. 180–190°; $C_4H_9Cl$ and trichlorethylene to $C_4H_8Cl_2$ ; T. 200°; chlorbutane is used as a solvent.	$AlCl_3$ ; using $Zn$ halide, the conversion occurs with less $Cl_2$ .	Konsortium für Elektrochemische Industrie G.m.b.H.: E.P. 453,414, Oct. 8, 1936.
Preparation of ethyl chloride; ethylene and $HCl$ in ratio 1 : 2; T. above 125°; better 200–325°.	Melts of metal chlorides, e.g., 60 parts $AlCl_3$ , 30 p. $NaCl$ and 10 p. $FeCl_3$ or 64 p. $AlCl_3$ and 34 p. $KCl$ .	Dow Chemical Co. (Amos): U.S.P. 2,140,500, Dec. 20, 1938.
Chlorination of ethylene chloride; ethylene chloride is led together with $Cl_2$ over the catalyst; ethylene chloride: $Cl_2 = 0.7 : 1.1$ ; T. 400–480°; yield, 20% 1,1-dichlorethylene; 21.7% 1,2-dichlorethylene; 29.2% trichlorethylene, and 28.5% other chlorination products.	Melt consisting of 60 p. $AlCl_3$ , 30 p. $NaCl$ and 10 p. $FeCl_3$ .	Dow Chemical Co. (Reilly): U.S.P. 2,140,548 and U.S.P. 2,140,549, Dec. 20, 1938.

Table 2 (Continued).

Reaction	Catalyst	Observer
Preparation of ethyl chloride; conversion in a continuous process of $C_2H_4$ and $HCl$ at about $10^\circ$ or below over the catalyst and an aliphatic chlorinated hydrocarbon at about 1 atm.; from this zone the reaction liquid containing the ethyl chloride formed is partially withdrawn and heated under diminished pressure so that ethyl chloride evaporates; the contact liquid is cooled again and led back in the reaction step; likewise ethylene-containing gases (cracking gases) may be worked out; as chlorinated hydrocarbons: ethylene chloride, 1,1,2-trichlorethane, tetrachlorethylene, acetylene tetrachloride, propylene chloride are suitable.	$AlCl_3$ .	Dow Chemical Co. (Pierce): U.S.P. 2,140,927, Dec. 20, 1938.
Chlorination of dichlorethylene to heptachloramylene; 2 mol $CCl_4$ + about 3 mol sym. dichlorethylene; between $45^\circ$ and the c.p. of the reaction mixture; the product may be further chlorinated under the influence of Hg-light arc or in the presence of $FeCl_3$ at $50^\circ$ ; after 5 days a colorless oil with camphor-like odor is obtained.	Friedel-Crafts catalysts.	Imperial Chemical Industries, Ltd. (Kirkbridge): E.P. 503,205, April 27, 1939.

Table 3. Catalytic Chlorination of Unsaturated Hydrocarbons.

Reaction	Catalyst	Observer
Chlorination of unsaturated hydrocarbons from industrial distillation gases in the presence of small amounts of $Cl_2$ gas below $120^\circ$ which compresses the chlorinated hydrocarbons.		Bergius: G.P. 298,492, Kl 12o, Gr 2, Aug. 27, 1923.
Chlorination of unsaturated hydrocarbons from cracking processes to alcohols; $HCl$ reacts with unsaturated hydrocarbons up to $C_7H_{14}$ , first at $70^\circ$ , then at $150^\circ$ (or the reverse).	$ZnCl_2$ , $SnCl_2$ , also $MoCl_5$ , $UCl_4$ , $SbCl_5$ , $WCl_6$ , $VCl_4$ , or $TiCl_4$ .	Piotrowski and Winkler: <i>Przemysl Chem.</i> , 15, 25 (1931).
Chlorination of olefins with $HCl$ to alkyl halides; T. $70$ – $100^\circ$ .	$Sn$ , $Zn$ on active charcoal (water decreases the yield of alkyl chlorides).	Piotrowski and Winkler: <i>Ibid.</i> , 15, 25 (1931). Piotrowski and Winkler: G.P. 574,802 (1932).
Chlorination of olefins; T. $250^\circ$ .	$Al_2O_3$ .	General Motors Corporation: U.S.P. 2,033,374. Gayer: <i>Ind. Eng. Chem.</i> , 25, 1122–1127 (1933).
Chlorination of unsaturated hydrocarbons.	A small quantity of olefin in the material to be chlorinated.	Deanesly: <i>J. Am. Chem. Soc.</i> , 56, 2501 (1934). Deanesly: B.P. 399,991 (1933).
Chlorination of olefins (3–7 C. atoms in molecule) to alkyl halides.	Active charcoal, silica gel, $Al$ gel in a mixture with metal halides.	Strange and Kane: E.P. 414,766 (1934). F.P. 769,103 (1934).
Chlorination of higher olefins (2–4 C atoms in molecule) with $HCl$ or $HBr$ .	Active charcoal, silicic acid gel.	I. G. Farbenindustrie A.-G.: F.P. 780,057 (1934).
Chlorination of unsaturated aliphatic hydrocarbons (3–5 C atoms in molecule) in presence of $Cl_2$ at $160^\circ$ under pressure.	$SbCl_5$ , $FeCl_3$ .	Dow Chemical Co. (Britton, Coleman and Hadler): U.S.P. 2,018,345, Oct. 22, 1935.
Chlorination of olefins or olefin mixtures (cracking gases) in the preparation of 1,2-dichlorethane or 2,3-dichlorbutane at $20$ – $120^\circ$ under normal or high pressure; reaction may be carried out in either liquid or gaseous phase.	Anhydrous $CaCl_2$ containing halides of metals: $Ba$ , $Sr$ , $Be$ , $Ni$ , $Fe$ , $Co$ , $Cu$ , $Pb$ , $Mo$ , $Al$ , $Sb$ .	Shell Development Co. (Kuys and Edwards): U.S.P. 2,099,231, Nov. 16, 1937.
Conversion of 1,2-dichlorbutene-3 (obtained by chlorinating 1,3-butadiene) into 1,4-dichlorbutene-2; temp. up to $50^\circ$ ; e.g., 2.5 p. of a melt obtained from 14 p. $AlCl_3$ and 16 p. $FeCl_3$ heated to $300^\circ$ are added to 50 p. of 1,2-dichlor-butene-3 at $5$ – $10^\circ$ with stirring; after heating to $10^\circ$ ; a little ice water is added, filtered, and distilled by fractionation; 30 p. unchanged and 61 p. of the final product obtained.	$AlCl_3$ , $FeCl_3$ , $TiCl_4$ , $ZnCl_2$ , alone, or in a mixture with other metal chlorides.	I. G. Farbenindustrie A.-G.: E.P. 505,573, June 8, 1939.

Table 3 (Continued).

Reaction	Catalyst	Observer
Chlorination of $C_3H_6$ (industrial process).		Ellis: U.S.P. 1,422,838. Ellis: <i>J. Soc. Chem. Ind.</i> , <b>41</b> , 686A (1922).
Chlorination of $C_3H_6$ .	Porous and adsorbing $Al_2O_3$ , floric acid earth and $Fe_2O_3$ containing $SiO_2$ .	Gayer: <i>Ind. Eng. Chem.</i> , <b>25</b> , 1122-1127 (1933).
Chlorination of $C_3H_6$ in the presence of HCl or HBr; T. 16°; yield: *22% isopropylchloride **97% isopropylchloride	*Silicic acid gel. **Adsorbent impregnated with metal chlorides: $FeCl_3$ , $ZnCl_2$ .	Brouwer and Wibaut: <i>Rec. trav. chim.</i> , <b>53</b> , 1001 (1934).
Preparation of alkyl chlorides; olefins converted with hydrogen halide acids; T. 100-250°; e.g., 4.5 vol. propylene and 3.5 vol. HCl are led at 150° through the catalyst; 70% of the theoretical amount of isopropyl chloride is obtained.	Grained catalyst consists of 80% $H_3PO_4$ (89%) and 20% kieselguhr.	Universal Oil Products Co. (Schaad): U.S.P. 2,144,816, Jan. 24, 1939.

Table 4. Catalytic Chlorination of Acetylene.

Reaction	Catalyst	Observer
Chlorination of $C_2H_2$ : $C_2H_2 + 2Cl_2 \rightarrow C_2H_2Cl_4$	$SbCl_3$ .	Askenasy and Mugdan: G.P. 154,657 (1903).
Chlorination of $C_2H_2$ .	Fe + sulfur chloride.	Salzberg and Neustassfurt: G.P. 174,068 (1904).
Chlorination of $C_2H_2$ .	$FeCl_3$ .	Hoffer and Mugdan: U.S.P. 985,528 (1910).
Chlorination of $C_2H_2$ to dichloroethylene; T. 160-190°.	Coke pieces 2-3 cm. grain size.	Chemische Fabrik Griesheim Elektron A.-G.: G.P. 264,006 (1913).
Chlorination of $C_2H_2$ in the presence of $Cl_2$ (mol ratio 1 : 2).	Bauxite, $Fe_2O_3$ .	Chemische Fabrik Griesheim Elektron A.-G.: G.P. 372,193 (1923).
Conversion of tetrachlorethane with $C_2H_2$ to dichloroethylene; T. 350°; yield, 35% dichloroethylene and 40% unchanged tetrachlorethane $C_2H_2Cl_4 + C_2H_2 \rightarrow 2C_2H_2Cl_2$ .	Ni or Ni cpds. on active charcoal.	Chemische Fabrik von Heyden A.-G.: G.P. 566,034 (1923). G.P. 567, 272 (1923).
Chlorination of $C_2H_2$ in the presence of HCl to vinyl chloride and ethylidene chloride at 200° for one hour per volume of catalyst; yield, 100 g. vinyl chloride and 8-10 g. ethylidene chloride; saponification of chlorobenzene into phenol accelerated by a mixture of $H_2O$ vapor and chlorophenol led over a catalyst at 500-550°.	Cpds. of Bi, Sb, Ba, Si, Mg, V, Al, Zn, Fe, C; $BiCl_3$ , $TiO_2$ , $ThO_2$ , $ZrO_2$ , $Al_2O_3$ , silica gel on active charcoal; $TiO_2$ and $SiO_2$ act the best.	Konsortium für Elektrochemische Industrie G.m.b.H.: E.P. 339,093, Dec. 4, 1930. Chackley: <i>J. Am. Chem. Soc.</i> , <b>51</b> , 2489 (1929).
Chlorination of $C_2H_2$ to dichloroethylene at room temp.: (1) 90-95% $C_2H_2$ and 5-10% $Cl_2$ to 90% dichloroethylene and 10% tetrachlorethane (only low-boiling <i>trans</i> -dichloroethylene); T. 40-50°. (2) initial T. 130°; working T. 160-180°.	(1) active charcoal, 1-2 mm. grain size; diameter of layer, 35 mm.; length of layer, 500 mm. (2) charcoal (a mixture of both stereoisomeric forms).	I. G. Farbenindustrie A.-G.: G.P. 553,149 (1932). E.P. 310,964 (1929). F.P. 674,254 (1929).
Chlorination of $C_2H_2$ in the preparation of tetrachlorethane and trichloroethylene; yield: (1) 78-81% $C_2H_2Cl_4$ (calculated to $C_2H_2$ ). (2) 88% $C_2H_2Cl_4$ .	(1) $FeCl_3$ but not Fe. (2) $SbCl_3$ .	Wajaschko and Kossenko: <i>Ukrain. Khim. Zhur.</i> , <b>12-35</b> (1932).
Chlorination of $C_2H_2$ and vinyl chloride in gaseous phase; reaction HCl and $HC \equiv CH$ catalyzed by $HgCl_2$ ; reaction HCl	$HgCl_2$ , $BiCO_3$ , $FeCl_3$ and $ZnCl_2$ on silica gel.	Wibaut and van Dalfsen: <i>Rec. trav. chim.</i> , <b>51</b> (4) 636 (1932).

Table 4 (Continued).

Reaction	Catalyst	Observer
and $\text{H}_2\text{C}=\text{CHCl}$ not catalyzed by $\text{HgCl}_2$ at 25–195° even with an excess of $\text{HCl}$ ; reaction $\text{HCl}$ and $\text{H}_2\text{C}=\text{CHCl}$ catalyzed by $\text{ZnCl}_2$ giving always $\text{C}_2\text{H}_5\text{C}=\text{CH}_2$ .		
Chlorination of $\text{C}_2\text{H}_2$ in the presence of $\text{HCl}$ and $\text{Cl}_2$ to 1,1,2-trichlorethane; T. 80–150°; yield, 90–95%; reaction mixture: 45% $\text{C}_2\text{H}_2$ , 40% $\text{HCl}$ , 5% $\text{Cl}_2$ , 10% inert gases.	Active charcoal, silica gel charged with metal salts.	I. G. Farbenindustrie A.-G.: G.P. 547,005 (1932).
Chlorination of $\text{C}_2\text{H}_2$ ; 90% $\text{C}_2\text{H}_2$ converted into tetrachlorethane, while only 1–2% $\text{H}_2$ is bound to $\text{HCl}$ ; reaction mixture: 12% $\text{C}_2\text{H}_2$ , 40% $\text{H}_2$ and $\text{CH}_4$ , $\text{HCl}$ , $\text{CO}$ , $\text{N}_2$ .	Fe catalyst treated with $\text{Cl}_2$ at 200°.	Ruhr Chemie A.-G.: F.P. 747,786, April 6, 1933.
Chlorination of $\text{C}_2\text{H}_2$ (11.6%) in the presence of large amounts of $\text{H}_2$ (43.0%) to tetrachlorethane; T. 700°; yield, 64.2% and 35.8% dichlorethylene.	Fe or cpds., such as $\text{FeCl}_2$ impregnated in silica gel (11.6%).	Ruhr Chemie A.-G. (Klein): G.P. 613,607 (1935).
Chlorination of $\text{C}_2\text{H}_2$ , the latter in the presence of non-combustible aliphatic chlor-hydrocarbons, such as $\text{CCl}_4$ , is brought into contact with the catalyst to form ethylene chloride, tetrachlorethylene, and $\text{CCl}_4$ .	Melts of metal chlorides, such as eutectic melts of $\text{AlCl}_3$ , $\text{NaCl}$ and $\text{FeCl}_3$ .	Dow Chemical Co. (Reilly): U.S.P. 2,140,551, Dec. 20, 1938.

Table 5. Catalytic Chlorination of Alkyl Chlorides.

Reaction	Catalyst	Observer
Chlorination of ethyl chloride to 1,1-dichlorethane; T. 250–400°.	Bone charcoal.	Damoiseau: <i>Bull. soc. chim.</i> (2), 27, 113 (1877).
Chlorination of ethyl chloride to hexachlorethane.	Charcoal.	Dow Chemical Co.: U.S.P. 1,437,636 (1924).
Chlorination of vinyl chloride in the presence of $\text{HCl}$ to 1,1-dichlorethane.	$\text{ZnCl}_2$ on active charcoal, silica gel or bleaching earth activated with $\text{HCl}$ .	Dow Chemical Co. (Wibaut and van Dalfsen): U.S.P. 1,990,968 (1934).
Chlorination of vinyl chloride by $\text{HCl}$ in non-aqueous phase at 10–135°; as reaction medium may be used inert liquids such as vinyl chloride, $\text{C}_2\text{H}_5\text{Cl}$ , and ethylidene chloride, $\text{C}_2\text{H}_2\text{Cl}_2$ .	$\text{AlCl}_3$ , $\text{FeCl}_3$ .	Dow Chemical Co. (Nutting, Petrie and Huschke): U.S.P. 2,007,144, July 2, 1935.
Chlorination of halide cpds. such as P.	$\text{ZnCl}_2$ , $\text{CuCl}_2$ .	N. V. Elektrochemische Industrie (Gaspar and Galissen): Austrian P. 126,559, Jan. 25, 1932; add to E.P. 302,927 (filed Dec. 22, 1927).
Chlorination of alkyl halides; di-alkyl ethers are brought to a reaction with hydrogen halides in the presence of water vapor at 260–400°, better at 300–370°, e.g., vapors of $\text{HCl}$ of a specific gravity 1.2 and diethyl ether in a volume relation of 12 : 7 are led at 360° over $\text{Al}_2\text{O}_3$ ; the reaction vapors are cooled further with water, then washed with alkali, dried with $\text{H}_2\text{SO}_4$ ; a 50% yield of ethyl chloride is obtained.	A catalyst acting as a dehydrating agent under high pressure between 15–20 atm.; suitable catalysts are: oxides, hydroxides and salts of $\text{O}_2$ -containing acids of metals of the 3rd or 4th group, such as Th, Zr, Ti, or Al, namely cpds. capable of dehydrating alcohols, e.g., dehydrated Al sulfate or Al oxide which with the addition of binding agents, such as water glass, forms stable molecules.	
Preparation of alkyl chlorides; olefins converted with hydrogen halide acids; T. 100–250°; e.g., 4.5 vol. propylene and 3.5 vol. $\text{HCl}$ are led at 150° through the catalyst; 70% of the theoretical amount of isopropyl chloride is obtained.	Grained catalyst consists of 80% $\text{H}_3\text{PO}_4$ (89%) and 20% kieselguhr.	Universal Oil Products Co. (Schaad): U.S.P. 2,144,816, Jan. 24, 1939.

Table 6. Catalytic Chlorination of Alcohols.

Reaction	Catalyst	Observer
Chlorination of $C_2H_5OH$ to $C_2H_5Cl$ (used in the preparation of tetraethyllead).		
Chlorination of $C_2H_5OH$ to $C_2H_5Cl$ ; $C_2H_5OH + HCl \rightarrow C_2H_5Cl + H_2O$	Active charcoal prepared with $H_3PO_4$ better than kieselguhr and charcoal.	I. G. Farbenindustrie A.-G. (Dachlauer and Eggert): G.P. 441, 747 (1927).
Chlorination of $CH_3OH$ in the presence of $Cl_2$ .	Silica gel, $Al_2O_3$ .	I. G. Farbenindustrie A.-G.: G.P. 503,716 (1930). Roessler and Hasslacher Chemical Co. (Carlisle): U.S.P. 1,834,089 (1932).

Table 7. Catalytic Chlorination of Acids.

Reaction	Catalyst	Observer
Chlorination of acetic acid.	P- $PCl_5$ -I.	Brückner: <i>Z. angew. Chem.</i> , <b>41</b> , 226 (1928). Brückner: <i>J. Am. Chem. Soc.</i> , <b>47</b> , 123 (1928).
Chlorination of acetic acid.	P-I- $PCl_5$ only active catalysts, I-Fe and $Sn_2Cl_2$ gave negative results.	Ljubarski: <i>Zhur. Priklad. Khim.</i> , <b>2</b> , 621-627 (1929).
Chlorination of acetic acid: $CH_3COOH + Cl_2 \rightarrow CH_3ClCOOH + HCl$	P, I, S, or their mixtures.	Chemische Fabrik vorm. Fahlberg (List and Co.): G.P. 219,242 (1907).
Chlorination of maleic anhydride in the presence of $Cl_2$ ; T. 130°; yield, 80%.	Fe (100 parts maleic anhydride to one part powdered Fe).	Leder: <i>Russ. P.</i> 43,419, June 30, 1935.
Chlorination of acids; halogen migration in C chains and rings under the action of $AlCl_3$ in which Cl migrates from chlorinated ketones or acids in the chain or in the ring to a place possibly far removed from CO or $CO_2H$ , but not toward $CH_3$ placed at the end.	$AlCl_3$ .	Nenitzescu and Gavai: <i>Ann.</i> , <b>519</b> , 260-71 (1935).
Chlorination of acetic acid by $Cl_2$ activated by an electric discharge (introduced into the acetic acid); T. 100°.	Red P; mixture of I, $PCl_5$ and red P; the red P becomes very active during the catalytic reaction and causes a considerable increase in the yield of monochloroacetic acid.	Isomura: <i>J. Electrochem. Soc. Japan</i> , <b>7</b> , 251-60 (1939).

Table 8. Catalytic Chlorination of Ethers.

Reaction	Catalyst	Observer
Chlorination of $(CH_3)_2O$ in the presence of trichloroacetic acid to $CH_3Cl$ , CO and HCl; T. 300°.	Fe, Al and Cd phosphate.	I. G. Farbenindustrie A.-G. (Andrussow): G.P. 634,549, Kl 120, Aug. 29, 1936. F.P. 799,582, June 15, 1936.
Chlorination of $(CH_3)_2O$ in the presence of benzal chloride to $CH_3Cl$ and benzaldehyde; T. 280°.	$Al_2O_3$ gel (grains).	I. G. Farbenindustrie A.-G. (Andrussow): G.P. 634,549, Kl 120, Aug. 29, 1936. F.P. 799,582, June 15, 1936.
Chlorination of $(C_2H_5)_2O$ in the presence of HCl and $H_2O$ to $C_2H_5Cl$ and CO; T. 270°; pressure, 25 atm.	Ce phosphate.	
Chlorination of $(C_2H_5)_2O$ in the presence of benzotrichloride and 0.5% $H_2O$ to $CH_3Cl$ , benzoic acid, benzoic anhydride and benzoic acid methyl ester.		
Chlorination of diphenyl ether at high temp.; the amount of $Cl_2$ used should be so calculated that not less than 4 nor more than 10 atoms react with the diphenyl ether.	$Cl_2$ carriers.	Dow Chemical Co. (Prutton): U.S.P. 2,165,813, July 11, 1939.

Table 9. Catalytic Chlorination of Ketones.

Reaction	Catalyst	Observer
Chlorination of ketones; chlorinated ethyl ketones and chlorinated vinyl ketones obtained from carbonic acid chlorides and vinyl chloride in the presence or absence of solvents such as CS <sub>2</sub> , petroleum ether and CCl <sub>4</sub> , <i>e.g.</i> , benzoyl chloride, the catalyst stirred with cooling, moisture eliminated and vinyl chloride simultaneously introduced, the reaction product decomposed with glacial acetic acid and HCl to phenyldichlorethyl ketone; from CH <sub>3</sub> COCl and vinyl chloride distilled under diminished pressure, chlorvinylmethyl ketone (80%) is formed.	AlCl <sub>3</sub> serves as a condensation agent.  10 parts AlCl <sub>3</sub> .	I. G. Farbenindustrie A.-G.: E.P. 466,891, July 8, 1937.

Table 10. Catalytic Chlorination of Benzene.

Reaction	Catalyst	Observer
Chlorination of benzene in the presence of Cl <sub>2</sub> .	Fe + FeCl <sub>3</sub> ; AlCl <sub>3</sub> .	Chemische Fabrik vorm. Fahlberg (List and Co.): G.P. 219,242 (1907).
Chlorination of benzene in the presence of O <sub>2</sub> to chlorobenzene; T. 300-600°.	Active charcoal.	Gremli: Austrian P. 108,421 (1928). Austrian P. 108,424 (1928).
Chlorination of benzene; no marked formation of chlorobenzene.	Bone charcoal charged with 70% Cl <sub>2</sub> .	Nikolajew: <i>Zhur. Obsheei Khim.</i> 1, 1035 (1933).
Chlorination of benzene to chlorobenzene.	Active charcoal, silica gel, Al <sub>2</sub> O <sub>3</sub> with precipitated Cu and metals of the 3rd to 8th groups of the Periodic System.	Badische Anilin- und Soda Fabrik (Wietzel and Dirksen): G.P. 420,500 (1925). Prah: F.P. 715,009 (1931).
Chlorination of benzene derivatives: 4,8-dichlorbenzanthrone in the presence of benzyl chloride to dichlorbenzylbenzanthrone.	Cu bronze.	I. G. Farbenindustrie A.-G.: G.P. 514,652, Aug. 20, 1925.
Chlorination of benzene derivatives at low temp.; Cl cpds. more pure than when chlorinated with other catalysts.	I with Fe, very active catalyst surpassing greatly the Cl carrier; 1% Fe (in optional form) + 1% I; I - Ni, I - Co, I - Sb, I - Zn, I - Bi, I - P and I - Sn gave no favorable results; no I removed with formation of HCl.	Fierz-David: <i>Naturwiss.</i> , 17, 13, (1928). Fei and Romatsu: <i>Mem. Coll. Sci., Kyoto Imp. Univ. (A)</i> , 10, 325-330 (1927).
Chlorination of benzene derivatives in the preparation of $\alpha$ -chloroethyl benzene; methyl alcohol, acetone, dimethyl aniline or styrene, or their solutions in inert solvents are treated with gaseous HCl in the presence of small amounts of catalytically active substances which are able to form addition cpds. resolving readily into their respective components.	Di-, tri- and polyhydrochlorides forming amines used as catalysts; with the use of CH <sub>3</sub> O and butanol as catalysts, care must be taken that HCl-methyl alcohol remains finely suspended in the hydrocarbon mixture by stirring during the reaction.	I. G. Farbenindustrie A.-G.: F.P. 745,533, May 12, 1933.
Nucleus chlorination of benzene derivatives of the type C <sub>6</sub> H <sub>4</sub> X, where X = H (halogen, alkyl or phenyl group) chiefly parachlor cpds. formed; solvents may also be present.	Mixture of S and SbCl <sub>3</sub> ; additions, such as Fe and Pb, recommended.	Dow Chemical Co. (Stoesser and Smith): U.S.P. 1,946,040, Feb. 6, 1934.
Chlorination of benzene derivatives: preparation of aralkyl halides, such as benzyl chloride from dibenzyl ether and treated with hydrogen halide acids in the presence of H <sub>2</sub> O; T. 80-120°; elevated or diminished pressure.	Halides of heavy metals, such as: ZnCl <sub>2</sub> , FeCl <sub>2</sub> , Fe bromide or iodide.	Hercules Powder Co. (Spurlin): U.S.P. 2,140,550, Dec. 20, 1938.



Table 10 (Continued).

Reaction	Catalyst	Observer
Chlorination of benzene with gaseous chlorine to <i>o</i> - and <i>p</i> -dichlorobenzene in the ratio of 2 : 1; by further chlorination to trichlorides, the <i>o</i> -isomers are chlorinated faster, so that only 1,2,4-trichlorobenzene is obtained; 1,2,3-trichlorobenzene was not detected.	Fe.	Silbermann and Slobodnik: <i>Zhur. Priklad. Khim. (U.S.S.R.)</i> , <b>10</b> , 1080-1085 (1937).
Chlorination of benzene to monochlorobenzene and very little of higher chlorination products at low temp., 200-225°, and short contact time.	Melts of metal chlorides, such as eutectic mixtures of $\text{AlCl}_3$ , $\text{NaCl}$ and $\text{FeCl}_3$ .	Dow Chemical Co. (Reilly): U.S.P. 2,140,550, Dec. 20, 1938.
Chlorination of hydrocarbons, for example, benzene, toluene, with 1-2 mol $\text{NOCl}$ ; T. 350°; from benzene to benzyl chloride; more $\text{NOCl}$ gives a mixture of benzyl chloride, benzal chloride and benzal trichloride; $\text{CH}_4$ is converted into $\text{CCl}_4$ and a little $\text{CCl}_3\text{H}$ with 8.7 mol $\text{NOCl}$ at 400°, while with 1 mol $\text{NOCl}$ at about 350° $\text{CHCl}_3$ is the chief product.		Solvay Process Co. (Moyer): U.S.P. 2,152,357, March 28, 1939.
Conversion of chlorobenzene with aqueous ammonia solutions; T. 180-220°; the velocity constant for 30% $\text{NH}_3$ solution in the presence of $\text{CuCl}$ is expressed by $\log K = 6.484 - 3606/T \pm 0.015$ , and for $\text{CuCl}_2$ by $\log K = 12.52 - 6520/T$ ; $\text{NH}_4\text{Cl}$ slows down the reaction solubility of chlorobenzene in aqueous $\text{NH}_3$ ; at 200° in 29% $\text{NH}_3$ , it is 13% of chlorobenzene; at 200° in 20% $\text{NH}_3$ , it is 6.4% of chlorobenzene.	$\text{CuCl}$ , $\text{CuBr}$ and $\text{CuCl}_2$ ( $\text{Cu-NH}_3$ interferes with the intermediate product formed); activation energy ( $\text{CuCl}$ ) is calculated at 180-220° to 16,800 cal.	Woroshzow and Koblew: <i>Zhur. Obshchei Khim.</i> , <b>8</b> (70), 1106-19 (1938); refer also to (C. 1935 I 3653).

Table 11. Catalytic Chlorination of Various Compounds.

Reaction	Catalyst	Observer
Chlorination of dimethyl sulfide to $\text{CCl}_4$ ; T. 100-200°.	In the presence or absence of a catalyst.	Shering-Kahlbaum A.-G.: G.P. 417,970, Kl 12o, Gr 2, Aug. 20, 1925.
Chlorination in the preparation of chloroform and tetrachlorethylene; T. 230-340°; $\text{CO} + 3\text{HCl} \rightarrow \text{CHCl}_3 + \text{H}_2\text{O}$ $2\text{CO} + 4\text{HCl} \rightarrow \text{Cl}_2\text{C} \cdot \text{CCl}_2 + 2\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3$ , $\text{NiO}$ and $\text{CuO}$ mixed catalyst.	Thurm: U.S.P. 1,590,265 (1926).
Chlorination with large surface contact substances.	Hydrated metals; by heating these metals to a dark red glow, the hydrated water is liberated under diminished pressure.	Rhenania-Runheim Verein Chemische Fabriken A.-G.: G.P. 443,020, Kl 12g, April 19, 1927.
Chlorination.		Pei and Romatsu: <i>Mem. Coll. Sci., Kyoto Imp. Univ. (A)</i> , <b>10</b> , 325-330 (1927).
Chlorination of toluene.		Silberrad and Parke: <i>J. Chem. Soc.</i> , <b>127</b> , 1724-1731 (1928).
Chlorination in the preparation of $\text{CCl}_4$ .		Stock, Lux and Wastrow: <i>Z. anorg. allgem. Chem.</i> , <b>195</b> , 149-157 (1931).
Chlorination.		Robinson-Bindley Processes, Ltd.: F.P. 734,210, March 25, 1932.
Chlorination of cymene; T. 40-70°.	Fe powder and small amounts of water-free halides of Fe, Ni, Al, Zn, P, S.	Canadian Electro Products Co., Ltd. (Blaikie): E.P. 387,335, Jan. 27, 1933. E.P. 387,323, Jan. 27, 1933.
Chlorination; a method whereby a gas is withdrawn from the circulation after a definite temp. has been established and then passed through a second reaction space.		I. G. Farbenindustrie A.-G.: G.P. 504,635, Kl 12g, Oct. 25, 1934.

Table 11 (Continued).

Reaction	Catalyst	Observer
Chlorination of naphthalene; T. 125-160°; afterwards treated with inert gases; T. 200-240°.		Rattscher and Minossenko: Russ. P. 41,513, Feb. 28, 1935.
Chlorination of crude naphthalene in the presence of Cl <sub>2</sub> gas for 12 hrs. at 77.9°; afterwards treated with CO <sub>2</sub> for 13 hrs. at 200-240°.		Rattscher and Minossenko: Russ. P. 41,513, Feb. 28, 1935.
Chlorination of aminoanthraquinone cpds. in the presence of nitrobenzene; to a solution of 50 parts AlCl <sub>3</sub> in 800 parts nitrobenzene and 100 parts 1-aminoanthraquinone is added with stirring for 1/2 hr. at 25-30°, 70 p. SO <sub>2</sub> Cl <sub>2</sub> ; after 3 hrs. at 40° 1-amino-4-chloranthraquinone containing 13.8-14.2% Cl <sub>2</sub> is removed by vapor.	AlCl <sub>3</sub> or FeCl <sub>3</sub> added in an amount to keep the chlorinated product in solution.	Dupont: U.S.P. 1,986,798, Jan. 8, 1935.
Chlorination of paraffinic waxes to white, solid monochlor cpds. (dichlor cpds. are slightly yellow liquids; plastic agent); high vacuum 10 <sup>-2</sup> to 10 <sup>-4</sup> mm. Hg.		Imperial Chemical Industries, Ltd. (Oekrent): E.P. 452,662, Sept. 24, 1936.
Chlorination of inorganic and organic cpds. with activated Cl <sub>2</sub> <i>in statu nascendi</i> (originating from inorganic cpds. and accelerated by the formation of SiCl <sub>4</sub> ); action of Cl <sub>2</sub> upon a mixture of Al silicate with C.	Chlorides adsorbed on C.	Kretsch: <i>Zhur. Obshchei Khim.</i> (U.S.S.R.), 7 (69), 1249-1262 (1937).
Chlorination of ketene.	Active charcoal, silica gel.	Eschenbach: G.P. 638,441 (1937).
Chlorination of diaralkyl ethers with hydrogen halide; T. greater than 100°; process may be carried out under pressure and also without a catalyst.	Heavy metal halides, such as ZnCl <sub>2</sub> , FeCl <sub>3</sub> .	Hercules Powder Co. (Fisher): U.S.P. 2,108,937, Feb. 22, 1938.
Synthesis of highly chlorinated hydrocarbons; formation of heptachloropropane, chloromethanes and chloroethylenes which react only partially; mono- and dichloro-methane do not react; reaction velocity increases from tetrachlor- to monochloro-ethylene; ethylene itself does not react even with highly activated Cl cpds.; higher condensation products and their formation ascribed to the formation of highly reactive chloropropenes formed from chloropropanes and loss of HCl by the formation of vicinal CCl <sub>3</sub> or CCl <sub>2</sub> ; chloropropanes do not react with chloroethylenes except pentachloropropane; several unsaturated Cl cpds. with AlCl <sub>3</sub> or CCl <sub>4</sub> ; vicinal groups are readily "coupled" to the double bond under the influence of reducing agents such as Cu bronze, SnCl <sub>2</sub> or CuCl <sub>2</sub> ; in this coupling reaction, highly colored cpds. (halogen cpds. cause the coloring) are formed which also occur in the coupling reactions with AlCl <sub>3</sub> at higher temp. when HCl is split off; with many polychlorine cpds. AlCl <sub>3</sub> forms colored cpds. which sometimes show a high reactivity; this reactivity is not owing to the occurrence of a colored addition compound or product; these addition products should be considered as causing the catalytic activity of AlCl <sub>3</sub> ; they dissolve in the reaction mixture and are doubtless polar cpds.; the organic ion of the polar complex is the primary reacting agent either as a free ion or as a part of the polar complex.	AlCl <sub>3</sub> .	Prins: <i>Rec. trav. chim.</i> , 51, 1065-1080 (1932). Prins and Engelhard: <i>Ibid.</i> , 54, 307-312 (1935).
Preparation of secondary and tertiary alkyl monochlorides from pure gaseous or liquid olefins or mixed with other hydrocarbons and HCl in the presence of metal chlorides; olefins brought into the reaction in a vapor state; olefins from which secondary and tertiary chlorides originate are led over two temps., e.g., first over highly heated catalyst; 100 cc. of the outlet gas from a cracking distillate with 12 mol % unsaturated hydrocarbons; 2% C <sub>2</sub> H <sub>4</sub> , 8% C <sub>3</sub> H <sub>6</sub> , 2% C <sub>4</sub> H <sub>8</sub> with a theoretical amount of HCl; 38.5 kg. chlorides obtained: 15.0 kg. C <sub>2</sub> H <sub>5</sub> Cl, 22.5 kg. C <sub>3</sub> H <sub>7</sub> Cl, 7.3 kg. C <sub>4</sub> H <sub>9</sub> Cl	Mixtures of chlorides of the 2nd group or polyvalent metals with a high surface activity; these metals converted during reaction into active chlorides in the presence of HCl (dry); active charcoal impregnated with 20% SnCl <sub>4</sub> at 150°.	

Table 11 (Continued).

Reaction	Catalyst	Observer
Direct chlorination of acenaphthene with $\text{Cl}_2$ in acetic acid, alcohol, ether and benzene; from 1 mol acenaphthene and 2 mols $\text{Cl}_2$ as chief product is obtained 4,5-dichloracenaphthene; with increase in $\text{Cl}_2$ amt. higher chlorinated acenaphthenes are obtained; yield of 4-chloracenaphthene 90% at $62-64^\circ\text{F}$ .; twice recrystallized to 4,5-dichloracenaphthene.	Fe, Al, Cu, Pb, and I.	Daschewski and Karischin: <i>Prom. Org. Khim.</i> , <b>14</b> , 109-113 (1937); refer also to Paillard and Fawarger: (C. 1933 II 1182).
Chlorination of cyclohexane to monochlorocyclohexane; temp. not above $40^\circ$ ; e.g., upon cyclohexane with 3% anhydrous $\text{SnCl}_4$ , dry $\text{Cl}_2$ acts in the presence of light at $40^\circ$ ; up to 38% $\text{Cl}_2$ is taken up; then fractionated and 89% of monochlorocyclohexane and 10% dichlorocyclohexane are obtained.	0.5-5% $\text{SnCl}_4$ and likewise under action of light.	Dupont (Levine and Cass): U.S.P. 2,154,049, April 11, 1939.
Preparation of glycerol dichlorhydrin-( $\alpha$ ) from $\text{HCl}$ and glycerin; inert substances, immiscible with water, such as dibutyl ether, ethylene dichloride, chlorobenzene, benzene, anisol, and $\text{CCl}_4$ , are used as solvents for glycerol dichlorhydrin-( $\alpha$ ).	$\text{HCOOH}$ , $\text{CH}_3\text{COOH}$	Dow Chemical Co. (Britton and Heindel): U.S.P. 2,144,612, Jan. 24, 1939.

## Catalytic Dechlorination in Organic Chemistry

Table 1. Catalytic Dechlorination.

Reaction	Catalyst	Observer
Dechlorination of $\text{CHCl}_3$ to $\text{CHCl}_2$ to $\text{CHCl}$ ; $\text{CHCl}_3$ to $\text{CHCl}_2$ and $\text{HCl}$ .	$\text{BaCl}_2$ , $\text{CaCl}_2$ .	Chemische Fabrik Griesheim Elektron A.-G.: G.P. 263,457 (1912).
Dechlorination of amyl chloride and sodium acetate to amyl acetate and $\text{NaCl}$ .	Cu salts.	Kaufler: G.P. 274,202 (1913). Koch: U.S.P. 1,374,666 (1921).
Dechlorination of benzoetrichloride and $\text{H}_2\text{O}$ to benzoic acid and $\text{HCl}$ .	Fe powder.	Schultze: G.P. 82,927 Kl 12 June 12 (1894). G.P. 85,493 Kl 12 Sept. 10 (1895).
Dechlorination of benzoetrichloride and $\text{H}_2\text{O}$ to benzoic acid and $\text{HCl}$ (industrial process).	$\text{ZnCl}_2$ .	Mathieson Alkali Works: U.S.P. 1,557,153 (1924).
Dechlorination of pinene chloride in the preparation of camphor.	$\text{CuO}$ .	Masumoto: <i>Mem. Coll. Sci., Kyoto Imp. Univ. (A)</i> , <b>10</b> , 165-189 (1926).
Dechlorination of unsaturated cpds. by removal of the halogen halide; process best effected at $300-500^\circ$ under atmospheric or diminished pressure; preparation of trimethyl-ethylene from isoamyl chloride; isoprene from chlorisoamylene; butadiene from dichlorbutane.	$\text{TiO}_2$ .	I. G. Farbenindustrie A.-G. (Cunradi and Ober): G.P. 565,160, May 24, 1930.
Dechlorination of benzoyl chloride to benzaldehyde (small yield).		Akabori and Suzaki: <i>Proc. Imp. Acad. (Tokyo)</i> , <b>5</b> , 255-256 (1930).
Conversion of dechlorinated mass is carried out with the streaming energy of the water to be dechlorinated, whereby the excess of $\text{Cl}$ contained in water enters into the dechlorinating arrangement and is sucked in by narrow capillaries placed in		Mushka: G.P. 549,415, Kl 85c, April 27, 1932.

Table 1 (Continued).

Reaction	Catalyst	Observer
the part of the dechlorinated mass acting long as dechlorinating agent.		
Dechlorination of 1,3-dichloropropane to propane, from which cyclopropane, having anesthetic value, is synthesized.	Na, Mg, Zn.	Hass, McBee, Hinds and Glue-senkamp: <i>Ind. Eng. Chem.</i> , <b>28</b> , 1178 (1936).

## Catalytic Bromination in Organic Chemistry

Table 1. Preparation of Bromine.

Reaction	Catalyst	Observer
Preparation of bromine; according to the Deacon process. HBr produced by organic bromination is converted with an excess of air according to the reaction: $4\text{HBr} + \text{O}_2 \rightarrow 2\text{Br}_2 + 2\text{H}_2\text{O}$ at 325–425°; from the reaction gases Br is washed out with water and condensed, distilled off with vapor and separated from the condensate; yield, 95–100%.	Cu; likewise Ni-Co-Mn-Th, and Ce catalysts may be used.	Dow Chemical Co. (Hooker, G. W.): U.S.P. 2,163,877, June 27, 1939.

Table 2. Catalytic Bromination of Olefinic Hydrocarbons.

Reaction	Catalyst	Observer
Bromination of $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$ .		Wibaut, Dickman and Rutgers: <i>Koninkl. Akad. Wetenschappen Amsterdam</i> , <b>33</b> , 481–495 (1924).
Bromination of $\text{C}_3\text{H}_4$ and $\text{C}_3\text{H}_6$ .		Wibaut, Dickman and Rutgers: <i>Rec. trav. chim.</i> , <b>47</b> , 497–555 (1928).
Bromination of $\text{C}_2\text{H}_4$ compounds in OH-free solvents.	HBr catalyzes the reaction energetically.	Williams and James: <i>J. Chem. Soc.</i> , <b>1928</b> , 343–347.
Bromination of $\text{C}_2\text{H}_4$ on glass surfaces; T. 16°; pressure, a few mm. to 100 mm. Hg; on glass vessels at 0–25°, the reaction is heterogeneous and consists essentially in a Br addition in certain cases when an excess of Br is present; polymerization of intermediate bromination products; the $\text{C}_2\text{H}_4 \cdot \text{Br}_2$ reaction is accelerated by the addition of water, and considerably more the greater the addition; certain experimental results indicate strong dependence of the reaction velocity upon Br pressure; slowing down of the reaction by poisoned glass splinters and inert gases indicates a chain reaction in the gas space; the transition of the reaction order from 2 to 1 is favored by a moistened vessel wall, high Br pressure and low temp.; the reaction velocity constant is independent of the ethylene pressure, but increases with an increase in the Br pressure.		Williams: <i>J. Chem. Soc.</i> , <b>1932</b> , 1747–1758, 1758–1765.
Bromination of $\text{C}_3\text{H}_6$ ; propylene does not react with a solution of HBr in $\text{CH}_3\text{COOH}$ —only when hydrocarbons are added; in the presence of $\text{C}_2\text{H}_4$ , propylene reacts readily with HBr in $\text{CH}_3\text{COOH}$ ; propylene does not react with an aqueous or an alcoholic solution of HBr.	Organic bromides, such as $\text{C}_2\text{H}_5\text{Br}$ , $\text{C}_2\text{H}_5\text{I}$ , $\text{C}_2\text{H}_5\text{Br}$ ; polar liquids, such as $\text{H}_2\text{O}$ , $\text{C}_2\text{H}_5\text{OH}$ , $\text{CH}_3\text{COOH}$ , which act as accelerators.	Ipatieff, Pines and Wackher: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 2398 (1934).
Bromination of $\text{C}_2\text{H}_4$ in the presence of HBr to ethyl bromide.	Metal bromides mixed with active charcoal, silica gel, aluminum gel.	Strange and Kane: E.P. 414,766 (1934). F.P. 769,103 (1934).
Bromination of $\text{C}_2\text{H}_4$ derivatives in the presence of $\text{Br}_2$ .	HBr formed in the course of the process (autocatalytic reaction); $\text{IBr}$ , $\text{SbBr}_3$ , HBr and quinoline.	Anantakrishnan and Ingold: <i>J. Chem. Soc.</i> , <b>1935</b> , 984–987. Anantakrishnan and Ingold: (Refer to C. 1931 n 2982).
Bromination of $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$ in the presence of a Br-air mixture in the ratio of 1 : 1300; an inert gas as carrier of $\text{Br}_2$ may be used.	C-containing.	Dow Chemical Co. (Boundy and Roush): U.S.P. 2,088,159, July 27, 1937.

Table 3. Catalytic Bromination of Acetylene.

Reaction	Catalyst	Observer
Bromination of $C_2H_2$ , gaseous vinyl bromide and allyl bromide in liquid phase.		Wibaut: <i>Rec. trav. chim.</i> , <b>50</b> , 313-334 (1931).
Bromination of $C_2H_2$ in the presence of HBr or addition of HCl; T. 60-70° $C_2H_2 + HBr \rightarrow CH_2=CHBr$ $C_2H_2 + HCl \rightarrow CH_2=CHCl$ it is assumed that $C_2H_2$ , under the influence of CuCl or CuBr, is converted into isoacetylene, and then a hydrogen halide added $CH \equiv CH \rightleftharpoons CH_2=C$ $CH_2=C + HCl \rightarrow CH_2=CHCl$	250 g. CuCl <sub>2</sub> . 100 g. NH <sub>4</sub> Cl. 300 cc. 15% HCl.	Koslow: <i>Zhur. Priklad. Khim. (U.S.S.R.)</i> , <b>10</b> , 116-118 (1937).

Table 4. Catalytic Bromination of Various Compounds.

Reaction	Catalyst	Observer
Bromination of $C_6H_6$ .	AlBr <sub>3</sub> .	Klages and Allendorf: <i>Ber.</i> , <b>31</b> , 1005 (1898).
Bromination of cinnamic acid in the presence of Br <sub>2</sub> .		Plotnikow: <i>Z. physik. Chem.</i> , <b>53</b> , 605 (1905). James and Robinson: (Refer to C. 1934 I 1312).
Bromination of cinnamic ethyl ester.	IBr, SbBr <sub>3</sub> .	Brüner and Fischler: <i>Z. Elektroch.</i> , <b>20</b> , 64 (1914).
Bromination of acids.	Acetyl bromide, a strong catalyst; catalytic action of acid halides.	Watson: <i>J. Chem. Soc.</i> , <b>127</b> , 2067-2082 (1925).
Bromination of vinyl bromide in the presence of HBr to 1,1-dibromethane (small yield); $C_2H_2$ with an excess of HBr gives a good yield of 1,1-dibromethane.	Silica gel.	Wibaut: <i>Rec. trav. chim.</i> , <b>50</b> , 313 (1931).
Bromination of saturated aliphatic hydrocarbon gases; the gas is passed through liquid bromine at constant temp. whereby mixtures of constant composition could be continuously prepared; by varying the temp. the Br concentration can be adjusted so as to give the maximum yield (greater than 90%) of alkyl bromide when passed over iron at 290-370°.	Fe.	Perelis: <i>Ind. Eng. Chem.</i> , <b>25</b> , 1160-1161 (1933).
Bromination of acetone in light and heavy H <sub>2</sub> O.		Reitz: <i>Z. Elektroch.</i> , <b>43</b> , 659-661 (1937).
Bromination of various cpds.; $C_2H_5Br$ when mixed with $C_2H_4Br$ and then $C_2H_5Br$ shows no activity in transference by the exchange of bromine isotopes; by adding AlBr <sub>3</sub> an active Br atom is transferred to $C_2H_5Br$ ; the same holds true for the action of $C_2H_5Br_2$ upon $C_2H_5Br$ and of $C_2H_5Br$ upon $CHBr_3$ .	AlCl <sub>3</sub> , AlBr <sub>3</sub> .	Brejneva, Roginsky and Shilinski: <i>Acta Physicochim. U.R.S.S.</i> , <b>6</b> , 744-747 (1937).
Bromination of allyl bromide in the presence of HBr.	Ferromagnetic catalysts: Fe filings, freshly reduced Ni (completely free from O <sub>2</sub> ); the catalytic action of ferromagnetic metals is parallel with the tendency to form metal carbonyls.	Urushibara and Takebayashi: <i>Bull. Chem. Soc. Japan</i> , <b>11</b> , 754-756, Nov., 1936. <b>11</b> , 798-801, Dec., 1936. <b>12</b> , 51-54, Jan., 1937. <b>12</b> , 138-144, March, 1937. <b>12</b> , 173-176, April, 1937.

Table 4 (Continued).

Reaction	Catalyst	Observer
Bromination of brombenzene, chlorbenzene and fluorbenzene in gaseous phase; transition from <i>o,p</i> -substitution type to <i>p</i> -type at 400–450°; yields of <i>o</i> -, <i>m</i> - and <i>p</i> -chlorbrombenzene: 375°: 28.4%, 21.0%, 51.4% 400°: 25.7%, 23.3%, 45.5% 425°: 25.1%, 41.8%, 35.0% 475°: 20.4%, 53.7%, 27.3% yields of <i>p</i> -fluorobrombenzene: 360°: 71.0% 400°: 65.0% 550°: 24.0% 600°: 23.0% the reaction velocity with FeBr <sub>3</sub> is so great that at 200° the reaction is in progress; T. 200–500°; the substitution type is a function not only of the nature of the atom already present in the benzene nucleus, but also of the reaction temp. and nature of the catalyst used.	Artificial graphite.	van Loon and Wibaut: <i>Rec. trav. chim.</i> , <b>56</b> , 815–838 (1937). Scheffer: <i>Ibid.</i> , <b>45</b> , 522 (1926).
Bromination of benzene.	BeBr <sub>2</sub> , MgBr <sub>2</sub> , ZnBr <sub>2</sub> and CdBr <sub>2</sub> catalysts are compared; the catalytic influence is found to be proportional to the atom masses with the exception of BeBr <sub>2</sub> which shows the highest catalytic activity.	Pajeau: <i>Compt. rend.</i> , <b>207</b> , 1420–1422 (1938).
Bromination of cyclohexanol to cyclohexyl bromide; yield 80–82%; and cyclopentanol to cyclopentyl bromide; yield 89%.	3 mol HBr and 1.5 mol H <sub>2</sub> SO <sub>4</sub> .	Grummit: <i>Org. Syntheses</i> , <b>19</b> , 88 (1939).

## Catalytic Fluorination in Organic Chemistry

Table 1. Catalytic Fluorination.

Reaction	Catalyst	Observer
Fluorination of aliphatic hydrocarbons in the presence of gaseous HF; reaction vessel made of noncorrosive material, such as Cr-Ni steel; pressure, high or diminished.	Sb in a liquid state.	Kinetic Chemicals, Inc. (Holt, Yonker and Laird): U.S.P. 2,058,453, Oct. 27, 1936.
Fluorination of organic cpds. in the presence of HF: CCl <sub>4</sub> → CCl <sub>3</sub> F + CCl <sub>2</sub> F <sub>2</sub> C <sub>2</sub> Cl <sub>6</sub> → C <sub>2</sub> Cl <sub>5</sub> F + C <sub>2</sub> Cl <sub>4</sub> F <sub>2</sub> C <sub>2</sub> Cl <sub>4</sub> → C <sub>2</sub> Cl <sub>3</sub> F + C <sub>2</sub> Cl <sub>2</sub> F <sub>2</sub> T. 75–100° C <sub>6</sub> H <sub>5</sub> Cl <sub>3</sub> → C <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> F <sub>2</sub> c.p. 165° benzotrichloride to benzofluorodichloride; T. 175° acetylchloride to acetylfluoride; T. 15–25°.	Metal halides of the 1st, 2nd, 5th, 6th, 7th and 8th groups of the Periodic System, also on carriers, such as active charcoal; SbCl <sub>5</sub> .	Kinetic Chemicals, Inc. (Daudt and Yonker): U.S.P. 2,062,743, Dec. 1, 1936.
Fluorination of C <sub>2</sub> H <sub>2</sub> in the presence of HF to vinyl fluoride.	HgO, HgCl <sub>2</sub> , HgF <sub>2</sub> .	I. G. Farbenindustrie A.-G. (Söll): G.P. 641,878, Kl 12o, Feb. 16, 1937.

## Catalytic Iodination in Organic Chemistry

Table 1. Catalytic Iodination.

Reaction	Catalyst	Observer
Iodination of C <sub>2</sub> H <sub>4</sub> (T. 100°); for chlorination by HCl higher temp. required.	Without a catalyst; porous bodies.	Berthelot: <i>Ann.</i> , <b>104</b> , 184 (1857); <b>115</b> , 114 (1860).
Iodination of acetone at 25°; reaction velocity depends on single ions; in case it originates from HC <sub>2</sub> O <sub>4</sub> , it is a linear function of conc.; the reaction velocity from H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> is likewise a linear function of conc. above 0.1, while that originating from H <sub>2</sub> gives a maximum value; in the first place, HC <sub>2</sub> O <sub>4</sub>	KHC <sub>2</sub> O <sub>4</sub> .	Dawson and Smith: <i>J. Chem. Soc.</i> , <b>1930</b> , 79–85.

Table 1 (Continued).

Reaction	Catalyst	Observer
in a conc. solution acts catalytically, and the undissociated acid in the less conc. solution dominates the catalytic action of $H_2$ (with increasing dilution in an increasing degree).		
Iodination of organic cpds.; the reaction between phoron and iodine in 50% alcohol seems to run through a keto-enol transformation; the relative catalytic action of the acetic acid molecule and the acetate ion are the greatest in the iodination of acetone and the smallest in the iodination of phoron; in between these two, lies the value for mesitylene oxide.	The first stages in the catalytic action of $HCl$ , $CH_3COOH$ and buffer acetate solution upon the reaction are very strongly influenced by auto-catalysis induced by the action of the solvent; this is more noticeable in the case of iodination of mesitylene oxide in a 5% alcoholic solution.	Dawson and Spivey: <i>Ibid.</i> , 1931, 2658-2665
Iodination of $CH_3I$ in the presence of $CHCl_3$ to $CHI_3$ and $Cl_2$ ; T. 290°.	$Al_2O_3$ .	I. G. Farbenindustrie A.-G. (Andrussow): G.P. 634,549, Kl 12o, Aug 29, 1936. F.P. 799,582, June 15, 1936.
Iodination of <i>o</i> -chlorphenol, <i>o</i> -cresol, salicylic acid, gallic acid, hydroquinone, resorcline, phenol, guaiacol, anisol, phenetol and <i>o</i> -nitrophenol with free and combined iodine at 20° and 30° respectively; the process is determined by the reaction: $RH + HOI \rightarrow RI + H_2O$ .	Oxidation agents in neutral solutions follow in series: $CaOCl_2$ , $H_2O_2$ , $HNO_3$ , $C_6H_5SO_2NCl_2$ in acid solutions; $CH_3C_6H_4$ , $SO_2NaNCl$ , $CaOCl_2$ , $K_2CrO_4$ , $H_2O_2$ , $KMnO_4$ , $C_6H_5SO_2NCl_2$ , $HNO_3$ ; calcium hypochlorite and chloramine are especially suitable for iodination.	Aldoschin and Tschalychjan: <i>Zhur. Obshchei Khim.</i> , 9, 748-52 (1939).
Halogenation of high polymer cpds. (up to molecular weight 500,000) obtained from isoolefins at low temp. (-10 to -100°); for halogenation the polymers are treated with halogen ( $Cl$ , $F$ , $Br$ , $I$ ) in gaseous or liquid phase; T. -50 to +100°; the high polymer is dissolved in a solvent or halogenated in an inert diluent; halogen content up to 50%; presence of light such as sun or ultraviolet rays desirable; the halogenated cpds. may be stabilized by addition of difficultly volatilized compounds, e.g., aromatic amines; the halogenated polymer product added to a lubricant conveys upon it high pressure properties; addition of $S$ , or $S$ cpds. acts similarly.	Condensation catalyst $BF_3$ .	Standard Oil Development Co.: F.P. 829,600, June 30, 1938.
	I. peroxide, halogenation catalysts.	

## PART XIV

## Catalytic Nitrogenation in Organic Chemistry

Table 1. Catalytic Nitrogenation.

Reaction	Catalyst	Observer
Nitrogenation of $CaC_2$ (industrial process) $CaC_2 + N_2 \rightleftharpoons CaCN_2 + C$	Charcoal, $KOH$ , $K_2CO_3$ .	Frank and Caro: G.P. 88,363 (1895). G.P. 108,971 (1898).
	$CaCl_2$ .	Polzenius: G.P. 163,320 (1901).
	$CaCN_2$ .	Cyanide Gesellschaft: G.P. 203,308 (1907).
Nitrogenation of $CaC_2$ .		Oono: <i>Bull. Chem. Soc. Japan</i> , 7, 287-297 (1932).
Nitrogenation carried out simultaneously with the splitting off of $CO_2$ .		Selden Co. (Jaeger): E.P. 309,024, May 29, 1929.

Table 1 (Continued).

Reaction	Catalyst	Observer
Nitrogenation of benzene in the vapor phase by $\text{NO}_2$ (ratio, 1 : 2); T. $310^\circ$ ; yield, 83%; $2\text{C}_6\text{H}_6 + 3\text{NO}_2 \rightarrow 2\text{C}_6\text{H}_5\text{NO}_2 + \text{NO} + \text{H}_2\text{O}$ favorable passage: $4.12 \times 10^{-2}$ up to $8.25 \times 10^{-2}$ g. benzene per hour per g. catalyst.	* Silica gel; pumice and $\text{TiO}_2$ , inactive.	McKee and Wilhelm: <i>Ind. Eng. Chem.</i> , <b>28</b> , 662-667 (1936).
Nitrogenation of toluene; T. $275^\circ$ .		
Nitrogenation of pyridine and quinoline.		Shorygin and Toptschijew: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>7</b> (69), 193-197 (1937). (refer to C. 1937 II 4038).
Nitrogenation of cellulose in the presence of $\text{HNO}_3$ , $\text{N}_2\text{O}_4$ .		Shorygin and Chait: <i>Ibid.</i> , <b>7</b> (69), 188-192 (1937).
Nitrogenation of Tetralin with $\text{HNO}_3$ to 1,3-dinitrotetraline; T. $0-5^\circ$ ; yield, small amount of viscous mass; 50 g. Tetralin for 1 hr. kept at $0-5^\circ$ , then 2 g. urea added and poured on ice, the mass obtained washed with water and extracted with ether, and fractionated <i>in vacuo</i> ; becomes brown and disintegrates.	75 g. $\text{H}_2\text{SO}_4$ ( $d=1.84$ ) + 50 g. $\text{HNO}_3$ ( $d=1.5$ ) (added dropwise).	Makakow, Semljanski and Bibischew: <i>Ibid.</i> , <b>7</b> (69), 1280-1283 (1937); refer also to Tetralin G.m.b.H.: G.P. 299,014, Kl 12o Gr 25, March 17, 1916. (Refer to C. 1919 IV 374).
Nitrogenation of glacial acetic acid or acetic acid anhydride to viscous mass formation; nitrogenation in pure $\text{HNO}_3$ follows without formation of a viscous mass; 26.4 g. Tetralin poured into 182 cc. $\text{HNO}_3$ ( $d=1.5$ ) at $6-14^\circ$ within 1-2 hr.; the mixture poured on ice; yellow crystals originate from the oil on standing and are recrystallized from methyl alcohol; 26.4 g. Tetralin treated with 90 g. $\text{HNO}_3$ ( $d=1.5$ ) gives a yield of 80%.		
Continuous nitration of hydrocarbons; lower paraffinic hydrocarbons, such as $\text{C}_2\text{H}_6$ , $\text{C}_3\text{H}_8$ and $\text{C}_4\text{H}_{10}$ are nitrated in gaseous phase with $\text{HNO}_3$ in a known manner (refer to U.S.P. 2,071,122; C. 1937 II 1445); if the unconverted hydrocarbons are to be led in a circle, the side products formed, like aldehydes, ketones, and olefins, interfere; the residual gases, therefore, after separation of side products, are set free from ketones and aldehydes by water, then purified from nitrogen oxides by washing with 70% $\text{H}_2\text{SO}_4$ ; then the unsaturated hydrocarbons are converted into saturated by hydrogenation at about $190^\circ$ over Ni, and then only led back into the nitrogenation zone.		Commercial Solvents Corporation (Hodge): U.S.P. 2,150,120 March 7, 1939. Commercial Solvents Corporation (Martin and Hodge): U.S.P. 2,150,123, March 7, 1939.
Nitrogenation of lower hydrocarbons in vapor phase with $\text{HNO}_3$ (the hydrocarbons are preheated so that the required amount of $\text{HNO}_3$ is volatilized; in this manner the nitrated mixture is definitely adjusted and mononitro products are obtained exclusively).		Commercial Solvents Corp. (Martin): U.S.P. 2,153,065, April 4, 1939.

## Catalytic Denitrogenation in Organic Chemistry

Table 1. Catalytic Denitrogenation.

Reaction	Catalyst	Observer
Denitrogenation of the diazo-compounds (industrial process).	Salts of Cu oxydul or Cu powder.	Sabatier: "Die Katalyse in der Organischen Chemie," p. 179. Sandmeyer: <i>Ber.</i> , <b>17</b> , 1635, 2652 (1884). Gattermann: <i>Ber.</i> , <b>23</b> , 1220 (1890).



Table 1 (Continued).

Reaction	Catalyst	Observer
Preparation of butyl amine and dibutyl amine from butanol and $\text{NH}_3$ ; the heated alcohol with the catalyst is sprayed into a container in which $\text{NH}_3$ is present; T. 215–225°; pressure 60–70 atms.	Dehydrating or hydrogenating.	Kodak, Ltd. (Hasche): E.P. 501,763, March 30, 1939.
Wurtz reaction: $2\text{C}_6\text{H}_5\text{I} + 2\text{Na} = \text{C}_6\text{H}_5\text{—C}_6\text{H}_5 + 2\text{NaI}$ ; conversion follows in evacuated tubes with Na powder in ether at 25°, and after treating the product with alcohol and water the NaI formed is titrated.	Benzophenone, tetraphenyl ethylene and acetophenone ketazine; as Na-transporting catalyst may serve only a substance which is able to take up 2 Na atoms more rapidly than to give them off again in the following reaction with the alkyl iodide, without being alkylated itself.	Talmud: <i>Zhur. Fiz. Khim.</i> , 11, 526–32 (1938).

## Catalytic Sulfurization in Organic Chemistry

Table 1. Catalytic Sulfurization.

Reaction	Catalyst	Observer
Sulfurization of anthraquinone (industrial process).	Hg and its salts.	Bayer: G.P. 149,801 (1902). G.P. 157,123 (1903).
Sulfurization of anthraquinone.	Hg (1%) or V salts (organo-mercuro cpds. formed which are decomposed by $\text{SO}_3$ ).	Meyer: <i>Compt. rend.</i> , 183, 519–521 (1926).
Sulfurization of anthraquinone.	Hg.	Meyer: <i>Bull. soc. chim.</i> (4), 41, 1627–1638 (1927).
Sulfurization of $\text{C}_2\text{H}_4$ (industrial process): $\text{CH}_2 : \text{CH}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_3\text{CH}_2\text{OSO}_3\text{H}$	Cpds. of Fe and Cu; $\text{AgSO}_4$ .	Damiens, de Loisy and Piette: G.P. 414,913 (1920). Glund and Schneider: E.P. 152,495 (1920). Bayer: E.P. 185,757 (1922).
Sulfurization of aromatic cpds.: benzene sulfonic acid.	$\text{CuSO}_4$ , $\text{HgSO}_4$ , $\text{V}_2\text{O}_5$ , $\text{Na}_2\text{SO}_4$ ; $\text{Na}_2\text{—Li}_2\text{SO}_4$ greater than $\text{Na}_2\text{SO}_4$ and $\text{V}_2\text{O}_5$ .	Ambler and Cotton: <i>J. Ind. Eng. Chem.</i> , 12, 968–969 (1920).
Sulfurization of organic cpds. (pure S cpds. in hydrocarbon solutions).	Ni.	Elgin: <i>Ind. Eng. Chem.</i> , 22, 1290–1293 (1930).
Sulfurization of organic cpds.; preparation of chlorethane sulfonate with $\text{ZnSO}_4$ in aqueous $\text{MeOH}$ ; the $\text{C}_2\text{H}_5\text{Cl}_2$ is made to react with metal sulfites in solution or in suspension at a temp. below the boiling point of the solvent.	Cu, $\text{CuSO}_4$ , $\text{BaCl}_2$ .	I. G. Farbenindustrie A.-G.: E.P. 360,558, May 9, 1930.
Sulfurization reactions: $\text{PhNO}_2$ with 20% $\text{H}_2\text{SO}_4$ (coml.) at 90° gives 3% <i>p</i> - and 97% <i>m</i> - $\text{SO}_3\text{H}$ derivatives and 25% <i>p</i> - and 75% <i>m</i> -isomers; $\text{BzOH}$ with 10% $\text{H}_2\text{SO}_4$ at 150° gives 14% <i>p</i> - and 86% <i>m</i> - $\text{SO}_3\text{H}$ derivatives and 5% <i>o</i> -, 26% <i>p</i> - and 69% <i>m</i> -isomers; $\text{PhSO}_3\text{H}$ with 20% $\text{H}_2\text{SO}_4$ at 200° gives 5% <i>p</i> - and 95% <i>m</i> - $\text{SO}_3\text{H}$ derivatives and 31% <i>p</i> - and 69% <i>m</i> -isomers.	5% Hg.	
Sulfurization of organic cpds. expressed in an increase in the reaction velocity; the yield of $\alpha$ -sulfonic acid increases with an increase in Hg; Hg introduced into the reaction is almost completely bound in hydroquinone and the sulfonates; in an $\alpha$ -sulfurization with Hg, $\text{HgSO}_4$ accumulates at the $\alpha$ -position in the form of an organo-mercuro cpd. which when replaced by the Hg salt residue is decomposed by $\text{SO}_3$ .	Hg and V salts.	Lauer: (refer to C1931 II 1285).

Table 1 (Continued).

Reaction	Catalyst	Observer
Sulfurization of organic cpds.; gases containing $\text{SO}_2$ are mixed with hydrocarbons, such as $\text{CH}_4$ , in a ratio of 2 atoms $\text{H}_2$ to 1 atom $\text{S}$ ; T. $700^\circ$ ; at $800-850^\circ$ , a complete conversion into $\text{H}_2\text{S}$ takes place: $4\text{SO}_2 + 3\text{CH}_4 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{S} + 2\text{H}_2\text{O}$	$\text{CaS}$ , $\text{BaS}$ , $\text{MgS}$ , $\text{MnS}$ (prepared from the corresponding sulfates; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ by dehydration and reduction with hydrocarbons above $600^\circ$ ).	United Verde Copper Co. (Rosenstein); U.S.P. 1,967,264, July 24, 1934.
Sulfurization of unsaturated terpenes with $\text{H}_2\text{S}$ in the presence of an oxidizing agent such as air; for the preparation of polysulfides, it is necessary to work in an $\text{O}_2$ -free atmosphere or to add antioxidants such as hydroquinone, $\alpha$ -naphthol, e.g., 30 p. by volume sulfopinene, 150 p. by volume $\text{H}_3\text{PO}_4$ (85%) and $\text{H}_2\text{S}$ are heated to $22^\circ$ (increased to $40^\circ$ ) under normal pressure for 18 hrs.; the product obtained contains 12.8% $\text{S}$ which corresponds to a yield of 68% mercaptans.	Dimethyl sulfate; metal sulfides, acidic or basic contact catalysts; active charcoal as a catalyst gives mercaptans (94.3%); thereby $\text{H}_3\text{PO}_4$ is used instead of $\text{H}_2\text{SO}_4$ .	Hercules Powder Co. (Borglin and Ott); U.S.P. 2,076,875, April 13, 1937.
Sulfurization of $\alpha$ -naphthylamine in 92.7% $\text{H}_2\text{SO}_4$ ; the content of naphthylamine sulfo- acids in the melt varies between 87 and 92% with a minimum for $\text{Cu}$ and a maximum without additions; the content of 1,2-isomers of naphthionic acid is slightly influenced by additions (maximum for $\text{Cu}$ ); the 1,5-isomer was found qualitative in all melts.	$\text{Fe}$ -, $\text{Cu}$ -, $\text{Al}$ -, $\text{Ni}$ -, $\text{Ag}$ -, and $\text{Hg}$ sulfates and $\text{V}_2\text{O}_5$ taken in amount of 0.02 mol per one mol $\alpha$ -naphthylamine.	Lenhold and Ssafronenko: <i>Zhur. Priklad. Khim.</i> , 11, 286-296 (1938).
Sulfurization of aromatic cpds. mechanism of the reaction; to avoid incomplete or too far-reaching sulfurization, the conc. of $\text{H}_2\text{SO}_4$ must be kept within definite limits; it is advantageous to keep it in the vicinity of the upper limit of $\pi$ -sulfurization.		Ufimzew: <i>Prom. Org. Khim.</i> , 4, 157-61 (1937).

## Catalytic Desulfurization in Organic Chemistry

Table 1. Catalytic Desulfurization of Benzene.

Reaction	Catalyst	Observer
Desulfurization of benzene and oils by hydrogenation in a stream of $\text{H}_2$ at 100 l/hr.; T. $340^\circ$ ; pressure, 100 atm.	$\text{Cu}$ , $\text{Co}$ , pumice.	Roberti: <i>Mem. accad. Lincei</i> , 2 (25), 5-15 (1930).
Desulfurization of benzene containing thiophene by destructive hydrogenation; benzene is not hydrogenated at $450^\circ$ in the presence of $\text{MoS}_3$ while thiophene is attacked; at $850^\circ$ , 90% $\text{C}_6\text{H}_4\text{S}$ decomposes $\text{C}_6\text{H}_4\text{S} \rightarrow \text{C}_6\text{H}_4 + \text{S} \rightarrow \text{BuSH}$	$\text{MoO}_3$ (changes to $\text{MoS}_2$ , which is stable).	Moldawski and Prokoptschuk: <i>Zhur. Priklad. Khim.</i> (U.S.S.R.), 5, 619-627 (1932).
Desulfurization of combustion benzene by pressure hydrogenation; Kaschpir benzene containing 10.6% $\text{S}$ is hydrogenated for one hour at $350^\circ$ under 80-90 atm. pressure in the presence of 3% $\text{H}_2$ .	10% $\text{MoS}_3$ ; better results obtained by using metals or metal oxides instead of sulfides; best desulfurization obtained with $\text{Cr}_2\text{O}_3$ or iron ore; activity of $\text{Cr}_2\text{O}_3$ increased by iron.	Nametkin, Ssanin, Makower and Zyba: <i>Khim. Tverdogo Topliva</i> , 4 (1), 44-50 (1934). Nametkin, Ssanin, Makower and Zyba: <i>Ibid.</i> , 5, 333-357 (1934).
Desulfurization of crude benzene; T. $200-300^\circ$ ; pressure, 10 atm. $\text{H}_2$	Sulfides of metals of the 6th to 8th groups: $\text{Co}$ , $\text{W}$ , $\text{Mo}$ , or $\text{Ni}$ on active charcoal or silicic acid gel.	I. G. Farbenindustrie A.-G. (Guthke); U.S.P. 1,932,369 (1933).

Table 1 (Continued).

Reaction	Catalyst	Observer
Desulfurization of Barsas saprolite (0.41% sulfur content) and Kaschpir benzine (10.98% S content) at 350° under ordinary pressure; Barsas saprolite desulfurized to 0.1% S content at 400°; action greater than hydrogenation; yield desulfurized benzene, 89.3%.	Equimolar solutions of Ni and Al nitrate precipitated with $\text{Na}_2\text{CO}_3$ ; precipitate mixed with one mol $\text{Al}_2\text{CO}_3$ and reduced at 350° with $\text{H}_2$ ; catalyst undergoes fatigue very rapidly as a result of adsorption taking place.	Titz, Schujkin and Epifanski: <i>Neflyanoe Khoz. (U.S.S.R.)</i> , <b>5</b> , 52-58 (1935).
Desulfurization of cracking benzene (S content decreased from 0.95% to 0.27%); T. 300°; pressure, 70 atm. (1000 lbs. sq.in.); a solution of thiophene in toluene containing 0.85% S is desulfurized by action with CO to COS; S content decreased to 0.05%; S content of a solution of thiophene in toluene in vapor phase at 300° under ordinary pressure is decreased from 0.60% to 0.32%.	$\text{MoS}_3$ .	Malishew: <i>J. Inst. Petroleum Tech.</i> , <b>22</b> , 341-346 (1936).
Desulfurization of S-containing benzenes and solutions of S cpds., such as ethyl mercaptan, butyl mercaptan, diethyl sulfide, dibutyl sulfide; T. 300-350°: (1) dehydrogenation as well as desulfurization of hydrocarbons (as the catalyst becomes poisoned, dehydrogenation stops and desulfurization proceeds); (2) at 350° the desulfurized product with small S content is led further over the poisoned catalyst and a considerable separation of $\text{H}_2\text{S}$ takes place.	Active charcoal with precipitated Pt (12%); after catalyst regenerates itself, it dehydrogenates and desulfurizes simultaneously.	Zelinsky and Schachnasarowa, <i>Izvest. Akad. Nauk S.S.S.R.</i> : 563-569 (1936).
Desulfurization of benzene (American method).	PbS suspended in NaOH.	Ssedych: <i>Neft</i> , <b>10</b> , 20-22 (1937).
Desulfurization of benzene at 1 atm. is unsatisfactory; at 400° and 20-40 atm. a far-reaching desulfurization is obtained with all catalysts; satisfactory results are obtained with $\text{MoS}_3$ at 350° in prolonged action; the refining loss by hydrogenation is about 4%; the content of benzene in unsaturated hydrocarbons becomes small; that in aromatics is practically unchanged; likewise the octane number; the S and resin content decrease considerably; a tendency to resin formation.	$\text{MoS}_3$ on aluminum gel; catalyst made of $\text{MgO}$ , $\text{ZnO}$ and $\text{MoO}_3$ ; and the $\text{MoS}_3$ formed.	Carlile and Cawley: <i>J. Soc. Chem. Ind.</i> , <b>57</b> , 347-49 (1938).
Desulfurization of benzenes consisting chiefly of olefins such as polymerization products from isobutylene: (1) by dissolving in large amount of 45-75% $\text{H}_2\text{SO}_4$ , T. 65-121° whereby only olefins dissolve and the insoluble S cpds. are separated and olefins precipitated from the acid on cooling; (2) by converting the benzenes into high antiknock benzenes by treating the separated olefins in the above manner and reforming the insoluble parts by catalytic treatment.		Standard Oil Development Co.: F.P. 827,762, May 3, 1938.
Desulfurization of benzenes by leading them in vapor phase over the catalyst up to T. 400°; S is removed from S cpds. as $\text{H}_2\text{S}$ ; simultaneously, however, cracking and polymerization of the unstable olefins take place; this reaction poisons the catalyst; to hinder it the benzenes must be led over the catalyst with high velocity, e.g., 3-50 volumes of benzene calculated with respect to the liquid per l. catalyst per hour.	Bauxite.	Phillips Petroleum Co. (Schulze): U.S.P. 2,162,319, June 13, 1939.

Table 2. Catalytic Desulfurization of Oils.

Reaction	Catalyst	Observer
Desulfurization of tar fractions.		Pertierra: <i>Anales soc. espan. fis. quim.</i> , 28, 1435-1450 (1930).
Desulfurization of crude oil in vapor phase at 380-450°; 80% desulfurized.	Fe ores (probably they may be regenerated in the apparatus); CuO and PbO do not work satisfactorily; anhydrous AlCl <sub>3</sub> gives better results; oxide mixture by Frascher: 75% CuO, 10% PbO, 25% Fe <sub>2</sub> O <sub>3</sub> .	Postowski and Kljuskin: <i>Neflyanoe Khim. (U.S.S.R.)</i> , 19, 561-564 (1930).
Desulfurization of naphtha.	Ni and Fe.	Elgin, Wilder and Taylor: <i>Ind. Eng. Chem.</i> , 22, 1284-1290 (1930).
Desulfurization of S cpds. and unsaturates (resins) in refined mineral oils; oil evaporated, polymerized over the catalyst, washed with alkali and redistilled.	O <sub>2</sub> , air, florida earth.	Stuart and Stuart: <i>E.P.</i> 367,848, March 24, 1932.
Desulfurization of S-containing crude hydrocarbons: tar oil (b.p. 188-275°); T. above 500°; the oil has a pleasant odor and a lower boiling point than before.	Metals of the Fe group or their mixture and alloys with other metals; Fe sponge placed in a tube and maintained at 600-700°.	I. G. Farbenindustrie A.-G.: <i>G.P.</i> 556,369, Kl 12r, Aug. 6, 1932.
Desulfurization of pressure hydrogenation oils boiling above 315°, especially mineral, tar and lubricating oils, at more than 30 atm. H <sub>2</sub> pressure.	Sulfides of the 6th group (freed from S and O cpds.).	<i>E.P.</i> 391,283, May 18, 1933. <i>F.P.</i> 743,816, April 7, 1933.
Desulfurization of a crude oil fraction; T. 440-480°; pressure, 85-100 atm. H <sub>2</sub> .	MoO <sub>3</sub> (NH <sub>4</sub> ) <sub>2</sub> MoS <sub>4</sub> , active charcoal+colloidal Mo acid; Cu chromite.	Pertierra: <i>Anales soc. espan. fis. quim.</i> , 31, 289-310 (1933).
Desulfurization of oil.	Fe hydroxide, silica gel and CuS on silica gel.	Holmes: <i>U.S.P.</i> 1,882,146 (1932).
Desulfurization of brown-coal tar, principally highly unsaturated oils only when the by-products are used for the preparation of fatty acids or soaps; EtSH is converted by O <sub>2</sub> mainly into ethane sulfonic acid and somewhat to Et <sub>2</sub> S <sub>2</sub> and Et <sub>2</sub> (SO); thiophene is converted completely into acid cpds. partly to H <sub>2</sub> SO <sub>4</sub> and CO <sub>2</sub> and partly to acid-containing S; PhSH is converted into Ph <sub>2</sub> S <sub>2</sub> to Ph <sub>2</sub> (SO); and finally to H <sub>2</sub> SO <sub>4</sub> ; benzyl sulfide is oxidized to benzyl sulfo-oxide and benzyl sulfone, then to H <sub>2</sub> SO <sub>4</sub> and CO <sub>2</sub> and possibly benzoic acid; the fuel and light oils yield no sulfonic acids with O <sub>2</sub> , indicating the absence of mercaptans.	Treatment with ozone.	Maneck: <i>Braunkohlenarch.</i> , 40, 53-90 (1933).
Desulfurization of light oils; T. 320-370°; time, 2-10 sec.	Bauxite.	Phillips Petroleum Co.: <i>Can. P.</i> 357,823 (1935).
Desulfurization of hydrocarbon oils; light-oil vapors passed at 310-400° in 2-10 sec. contact time; S content decreased by 25-40%, using bauxite, and by 20%, using fuller's earth.	Bauxite, fuller's earth (regenerated with water vapor at 425-450°); vanadite or chromite and especially crude ores.	Phillips Petroleum Co. (Buel and Schulze): <i>U.S.P.</i> 2,016,271 and <i>U.S.P.</i> 2,016,272, Oct. 8, 1935.
Desulfurization of oil fractions (Tschimbajew) under ordinary pressure.	40% Ni catalysts (20% and 60% Ni content less suitable).	Titz and Jurjew: <i>Uchenye Zapiski Gosud. Univ.</i> 6, 359-363, 365-374 (1936).
Desulfurization of hydrocarbon oils by refining through hydrogenation; T. 220-500°, ordinary or high pressure, the same method may be applied to the desulfurization of gaseous hydrocarbons (cracking gases); T. 500-750°.	Na <sub>2</sub> Mo <sub>2</sub> S <sub>7</sub> · (H <sub>2</sub> O) <sub>x</sub> or thiotungstate; instead of alkalis, salts of Cu, Ag, Au, Sr, Ba, Mg, Zn, Cd, Hg, Ce, Sn, Pb, Mn, Fe, Co, Ni, Pt may be used.	Universal Oil Products Co. (Grosse): <i>U.S.P.</i> 2,029,100, Jan. 28, 1936.
Desulfurization of mineral oil distillates; T. 283-393°; pressure, 3.5 atm. H <sub>2</sub> .	Highly porous active substances.	Standard Oil Co.: <i>U.S.P.</i> 2,060,091 (1936).
Desulfurization of California pressure distillates.	Na aluminate, NiO, CoO.	Ipatieff and Corson (Univ. Oil Products Co.)

Table 2 (Continued).

Reaction	Catalyst	Observer
Desulfurization of hydrocarbon oils.	Fuller's earth used as an adsorption agent to which is added metal salts (reacting with S cpds. to form sulfides) such as $\text{CuO}$ , $\text{CuCl}_2$ , $\text{CuNO}_2$ , $\text{HgCl}_2$ , $\text{FeCl}_3$ , $\text{Fe}_2(\text{SO}_4)_3$ , $\text{Cu}_2\text{O}$ , $\text{Cu}(\text{NO}_3)_2$ , $\text{FeCl}_3$ , $\text{FeSO}_4$ , $\text{CoCl}_2$ , $\text{CdCl}_2$ , $\text{Hg}(\text{NO}_3)_2$ , $\text{HgNO}_2$ , $\text{Cu}(\text{OH})_2$ , $\text{Cu}(\text{CO})_2$ , $\text{Cu}(\text{CH}_3\text{COO})_2$ , $\text{MgO}$ , $\text{Mg}(\text{OH})_2$ ; to the solid adsorbent is also added a strong oxidizing agent such as a Mn cpd., or refining is carried out by passing air or $\text{O}_2$ ; Cl loss of the catalyst is prevented by adding 0.01 cu. in. $\text{HCl}$ per barrel oil; suitable catalysts are: 90% dry ton, 5% $\text{CuCl}_2$ , 5% $\text{KMnO}_4$ ; 95% ton, 5% $\text{CuCl}_2$ , or 1-8% $\text{HgCl}_2$ ( $\text{CoCl}_2$ , $\text{CdCl}_2$ ), 1-30% $\text{CuCl}_2$ , and the remainder ton; the catalyst should contain not above 8% water; $\text{PbO}$ and $\text{NaOH}$ with 45-90% fuller's earth may be used.	Bennett-Clark Co. (Hoover): U.S.P. 2,042,050, Aug. 10, 1935. U.S.P. 2,042,051 to U.S.P. 2,042,054, May 26, 1936.
Desulfurization of hydrocarbon oils in steps by destruction of aliphatic S cpds. in vapor phase over catalysts; T. 315-425°; the $\text{H}_2\text{S}$ formed is washed with water under pressure and the cyclic S cpds., such as thiophene, are removed at 400-595°, whereby as catalysts serve oxides or sulfides of Fe, Co, Ni, Cu, Cr, Mo, W, V, Cd, Zn.	Fuller's earth, bentonite, bauxite, or the oxides of W, Mo, Cr, V, Cd, Zn.	Phillips Petroleum Co. (Schulze): U.S.P. 2,151,721, March 28, 1939.

Table 3. Catalytic Desulfurization of Organic Compounds; Removal of Thiophene.

Reaction	Catalyst	Observer
Desulfurization of S-containing organic cpds.; removal of thiophene from xylene-thiophene mixtures in the presence of $\text{H}_2$ under atmospheric pressure.	Na aluminate; metal sulfides and oxides.	Ipatieff and Schaad (Univ. Oil Prod. Co.) Ipatieff and Komarewsky (Univ. Oil Prod. Co.)
Desulfurization of S-containing organic cpds.; removal of thiophene from benzene; benzene not hydrogenated in the presence of $\text{MoO}_3$ at 350°; about 90% thiophene decomposed within 1 to $\frac{1}{2}$ hrs. hydrogenation; the thiophene ring decomposes thus: thiophene to tetrahydrothiophene to butyl mercaptan, the latter either hydrogenating to $\text{C}_4\text{H}_{10}$ and $\text{H}_2\text{S}$ , or splitting to $\text{C}_4\text{H}_8$ and $\text{H}_2\text{S}$ .	$\text{MoS}_2$ .	Moldawski and Prokoptschuk: <i>Zhur. Priklad. Khim.</i> (U.S.S.R.), 5, 619-627 (1932).
Desulfurization of S-containing organic cpds.; removal of thiophene (combined S) from liquid fuels in the presence of $\text{H}_2$ ; highest desulfurization degree (78%) reached with $\text{NiO}$ and $\text{CoO}$ at 400°; remaining S cpds. readily removed.	A mixture of $\text{NiO}$ and $\text{CoO}$ ( $\text{Ni}$ catalyst, most active); $\text{Al}_2\text{O}_3$ , $\text{MgO}$ , $2\text{CoO}$ , $3\text{MoO}_3$ .	Orloff and Brown: <i>Khim. Tverdago Topliva</i> , 3, 817-824 (1933).

Table 4. Catalytic Desulfurization of Gases and Liquids; Removal of Hydrogen Sulfide.

Reaction	Catalyst	Observer
Desulfurization of S-containing gases: the gas is first freed of $\text{H}_2\text{S}$ and then led over catalysts, the remaining S being converted into $\text{H}_2\text{S}$ in the presence of $\text{H}_2$ .	Au, Ag.	Fischer: E.P. 282,634, Feb. 15, 1928.
Desulfurization of S-containing gases: the $\text{H}_2\text{S}$ is converted into $\text{SO}_2$ and the bisulfite washed out of the gas with an alkali agent.	Catalysts containing heavy metals: Ni, Fe, Co, Cu, with addition up to 10% of a second metal: Pb, Bi, Cu, alkalies or alkaline earths; metals or metalloids of the 4th, 5th, or 6th group, or Cr, V, Si, C, Mo added.	I. G. Farbenindustrie A.-G.: E.P. 319,396, Oct. 17, 1929.

Table 4 (Continued).

Reaction	Catalyst	Observer
Desulfurization of S-containing gases; removal of H <sub>2</sub> S.	Cu.	(Univ. Oil Prod. Co.) Ipatieff and Corson
Desulfurization of S-containing gases; the H <sub>2</sub> S is removed from the circulating hydrogenation gas by pressure and washed with water first freed from mineral oil up to 0.3%.		Reichenbach: <i>Metallbörse</i> , 21, 1657-1658, 1689-1690 (1931).
Desulfurization of S-containing gases; removal of H <sub>2</sub> S and hydrocarbon impurities; T. 350-600°; combustion of hydrocarbons carried out with CO <sub>2</sub> in the presence of water vapor, the H <sub>2</sub> in H <sub>2</sub> S forming H <sub>2</sub> O	Large surface catalysts used to support the combustion process.	Zahn and Co. G.m.b.H. (Dreyer): E.P. 473,248, Nov. 4, 1937. F.P. 820,710, Nov. 16, 1937.
Desulfurization of S-containing liquids; removal of H <sub>2</sub> S by heat; combustion of H <sub>2</sub> S carried out in such a manner that the heat produced is used to remove gases from liquids charged with H <sub>2</sub> S; the process may be so conducted that by the use of a corresponding amount of air, S or SO <sub>2</sub> is formed; pressure may be used.	Usual catalysts.	I. G. Farbenindustrie A.-G.: E.P. 474,649, Dec. 2, 1937.
Desulfurization of liquids and gases (in particular, removing CS <sub>2</sub> ). $(C_3H_7)NCS \cdot S_2Mg + 2H_2O \rightarrow C_3H_7NCS \cdot SNH_2 + C_3H_7O + Mg(OH)_2 + CS_2$	Adsorption agent, Ca pentamethylenedithiocarbamate (slow reaction with a mixture consisting of piperidine pentamethylenedithiocarbamate and magnesia).	Mitchell and Parkes: <i>J. Soc. Chem. Ind.</i> , 57, 113-116 (1938).
Desulfurization of gaseous hydrocarbons, especially removing organic S cpds.; the precipitated S is regenerated by using solvents or distilling off with water vapor.	Active charcoal to which may be added metals or organic metal cpds.	Société Industrielle des Carburants et Solvants: F.P. 828,782, May 30, 1938.
Desulfurization (removing organic S cpds.) from H <sub>2</sub> S-free gases; T. 570-650°; the originating H <sub>2</sub> S is removed by moistening and then by means of dry lime.	Cu.	Kohle u. Eisenforschung G.m.b.H.: E.P. 491,299, Sept. 29, 1938.
Desulfurization of gases (led through the catalyst); T. 300-600°; H <sub>2</sub> S removed in the usual manner.	Metal thiomolybdate.	Maxted: E.P. 490,775, Sept. 15, 1938.
Desulfurization of gases freed of H <sub>2</sub> S and containing organic S cpds. in the presence of 0.4-1.0% O <sub>2</sub> ; T. 200-350°; the gas is preheated to 180° and then led over the catalyst.	Co or Ni (obtained by reduction of hydroxides of Ni or Co by coal distillation gas at 350°).	Gas Light and Coke Co. (Griffith and Plant): E.P. 489,398, Aug. 25, 1938.

Table 5. Catalytic Desulfurization of Hydrocarbons.

Reaction	Catalyst	Observer
Desulfurization of hydrocarbons above 300° under H <sub>2</sub> pressure; simultaneous cracking takes place when wood, charcoal, coke powder, or fuller's earth is added.	Alkali metals.	Erdöl- und Kohlenverwertung A.-G. (Berlin): G.P. 469,228, Cl 12o, Gr 1, Dec. 13, 1928.
Desulfurization of light hydrocarbons in vapor phase.	Active charcoal mixed with pieces of metal subjected to ultraviolet rays.	Magnus: G.P. 500,718 (1929).
Desulfurization of hydrocarbons; removal of thiophene from crude naphthalene by reduction to H <sub>2</sub> S; T. 300°; 50-100 atm. H <sub>2</sub> pressure.	Oxides precipitated on porous substances such as charcoal, kieselguhr, silica gel; NiO + Cr <sub>2</sub> O <sub>3</sub> on grained charcoal in the ratio of 10 : 1.	Koern: <i>Technika Ajakiri</i> , 9, 166 (1930).
Desulfurization of hydrocarbons, such as petroleum and asphalt, under H <sub>2</sub> pressure; thus the formation of large amounts of gaseous reaction products is avoided.	Mo catalyst; MoO <sub>3</sub> precipitated on active charcoal.	N. V. de Bataafsche Petroleum Mij: Jugoslavia P. 9,950, May 4, 1931.

Table 5 (Continued).

Reaction	Catalyst	Observer
Desulfurization of hydrocarbons; removal of $\text{SO}_2$ from vapor kettle heated gases; washing out of outlet gases by the addition of $\text{Mn}''$ in conc. of 0.025% recommended.	Metal ions $\text{Mn}''$ and $\text{Fe}''$ act as positive catalysts; $\text{Cu}''$ acts as a negative catalyst; $\text{Zn}''$ , $\text{Ni}''$ and $\text{Ca}''$ do not influence the action of $\text{Mn}''$ .	Johnston: <i>Ind. Eng. Chem.</i> , <b>23</b> , 559-561 (1931).
Desulfurization of hydrocarbons; purification of products containing $\text{O}_2$ and resulting from catalytic hydrogenation of hydrocarbons; T. 100-300°; pressure, 50 atm.; hydrogenation products containing 0.07% S subjected to 200 atm. $\text{H}_2$ pressure.	Difficultly reducible oxides or S cpds. of the heavy metals of the 1st, 2nd, 3rd, 4th, 5th, 6th or 8th group, or a mixture of O and S cpds.; catalyst obtained from Ni sulfide and W sulfide (Ni tungstate treated with $\text{H}_2$ ).	E.P. 391,283, May 18, 1933. F.P. 743,810, April 7, 1933.
Desulfurization of hydrocarbons; hydrocarbon vapors are passed with high velocity over the catalyst to prevent their decomposition; T. 400-600°.	Active charcoal.	Continental Oil Co. (Zurcher): U.S.P. 1,884,495 (1933).
Desulfurization of hydrocarbons containing S cpds.	S-combining metal oxides.	Silica Gel Corporation (Connolly): U.S.P. 1,886,261 (1932).
Desulfurization of hydrocarbons; decreasing the S content of coke by the addition of catalytic substances; if coal contains much organic S, desulfurization is smaller; a temp. of 900° should not be exceeded.	90% $\text{Cr}_2\text{O}_3$ and 10% $\text{MnCl}_2$ ; both salts decrease the S content in an amount up to 0.1%.	Gekhalit: <i>Zhur. Priklad. Khim.</i> (U.S.S.R.), <b>7</b> , 934-938 (1934).
Desulfurization of hydrocarbons according to the method of destructive hydrogenation.		Moldawski: <i>Destriktionaja Gidrogenisazija Topliva</i> , <b>1</b> , 168-182 (1934).
Desulfurization of hydrocarbons; removal of ethyl mercaptan from a cracked naphtha fraction at 250°; distillate cooled up to 45°; non-condensable part converted into thioether; at 400° and after 16 hrs., 40-45% ethyl mercaptan converted into thioether.	90% $\text{CdS}$ , 5% $\text{ZnS}$ and 5% $\text{Al}_2\text{O}_3$ ; active charcoal.	Standard Oil Development Co. (Huffmann and Whiteley, Jr.): U.S.P. 1,995,612, March 26, 1935.
Desulfurization of hydrocarbons; removal of S from California cracked gasoline in the presence of $\text{H}_2$ under atmospheric pressure.	$\text{Na}_2\text{Al}_2\text{O}_4$ $\text{Na}_2\text{Al}_2\text{O}_4 + \text{Na}$ sulfide $\text{Na}_2\text{Al}_2\text{O}_4 + \text{Mo}$ oxide $\text{Mo}$ oxide + $\text{CuO}$ $\text{Ni}_2\text{O}_3 + \text{alumina}$ $\text{NiO} + \text{alumina}$ $\text{Ni}_2\text{O}_3 + \text{Na}_2\text{Al}_2\text{O}_4$ $\text{Fe}_2\text{O}_3 + \text{alumina}$ $\text{MnO}_2 + \text{Na}_2\text{Al}_2\text{O}_4$ $\text{Ni}_2\text{O}_3 + \text{alumina} + \text{Na}_2\text{Al}_2\text{O}_4$ $\text{NiO} + \text{alumina} + \text{Na}_2\text{Al}_2\text{O}_4$	Ipatieff and Schaad: U.O.P.
Desulfurization of hydrocarbons; removal of S from California cracked gasoline under superatmospheric pressure in the presence of $\text{H}_2$ mixed with $\text{CO}_2$ , $\text{CH}_4$ , $\text{CO}$ and $\text{H}_2\text{O}$ vapor.	(1) 90% $\text{Ni}$ thiomolybdate 10% $\text{Na}_2\text{Al}_2\text{O}_4$ (2) 75% $\text{Ni}$ thiomolybdate 10% $\text{Na}_2\text{Al}_2\text{O}_4$ 15% diatomaceous earth (3) 50% $\text{Ni}$ thiomolybdate 10% $\text{Na}_2\text{Al}_2\text{O}_4$ 40% diatomaceous earth	Ipatieff and Schaad: U.O.P.
Desulfurization of hydrocarbons; removal of S from California cracked gasoline in the presence of $\text{H}_2$ under superatmospheric pressure.	(1) $\text{Ni}$ thiomolybdate (2) $\text{Ni}$ oxide + alumina + $\text{Na}_2\text{Al}_2\text{O}_4$ (3) $\text{CuO} + \text{alumina}$ (4) $\text{Ni}$ thioantimonate (5) $\text{Fe}_2\text{O}_3$ (6) $\text{Ni}$ thiomolybdate + $\text{Sb}_2\text{O}_3$ (7) $\text{Ni}$ thiomolybdate + $\text{CuO} + \text{alumina}$ (8) $\text{NiS} + \text{MoS}_2$ (9) 75% $\text{Ni}$ thiomolybdate 25% $\text{Na}_2\text{Al}_2\text{O}_4$ (10) 90% $\text{Ni}$ thiomolybdate 10% $\text{Na}_2\text{Al}_2\text{O}_4$ (11) 54% $\text{Ni}$ thiomolybdate on pumice	Ipatieff and Schaad: U.O.P.

Table 5 (Continued).

Reaction	Catalyst	Observer
	(12) 75% Ni thiomolybdate 10% $\text{Na}_2\text{Al}_2\text{O}_4$ 15% diatomaceous earth	
	(13) 50% Ni thiomolybdate 10% $\text{Na}_2\text{Al}_2\text{O}_4$ 40% diatomaceous earth	
	(14) 63% Ni oxide 17% alumina 10% $\text{MoS}_2$ 10% $\text{Na}_2\text{Al}_2\text{O}_4$	

Table 6. Catalytic Desulfurization of Gases; Purification of Gaseous Mixtures.

Reaction	Catalyst	Observer
Desulfurization of gases; purification of gases containing ingredients which reduce sulfide cpds.	Oxidation of $\text{H}_2\text{S}$ by $\text{O}_2$ or air.	I. G. Farbenindustrie A.-G.: G.P. 476,286, Kl 26d, May 13, 1929. F.P. 652,243, June 31, 1929.
Desulfurization of gases; purification of $\text{H}_2$ used for the hydrogenation of unsaturated cpds. containing S.	Alloys of Hg, Pb, Cd melted.	E.P. 306, 803 April 24, 1929. Can. P. 296,913, Jan. 21, 1930.
Purification of gases; removal of S from $\text{SO}_2$ containing gases: $2\text{SO}_2 + 4\text{H}_2\text{S} \rightleftharpoons 4\text{H}_2\text{O} + 3\text{S}_2$ (in a gaseous phase) $\text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 3\text{S} + 2\text{H}_2\text{O}$ (in a gaseous solution)	Active charcoal; good catalyst even at room temp.; coke less active than bauxite; silica gel permits complete conversion at room temp.; Fe ore with 14.1% $\text{Al}_2\text{O}_3$ and 80% $\text{Fe}_2\text{O}_3$ reacts well.	Juschkevitch, Karshawin and Awdejewa: <i>Zhur. Khim. Prom. (U.S.S.R.)</i> , 9 (3) 17-26 (1932).
Desulfurization of gases; purification of gaseous mixtures containing $\text{H}_2\text{S}$ , $\text{CO}_2$ , $\text{NH}_3$ and CN cpds. catalytically treated; $\text{H}_2\text{S}$ converted into $\text{SO}_2$ and $\text{SO}_3$ ; $\text{CO}_2$ into CO; $\text{NH}_3$ into $\text{HNO}_3$ and $\text{H}_2\text{SO}_4$ , as well as ammonium salts; CN into $\text{NH}_3$ ; valuable products obtained from washed alkalis of industrial gases: $(\text{NH}_4)_2\text{SO}_3$ , $(\text{NH}_4)_2\text{SO}_4$ .		I. G. Farbenindustrie A.-G. (Bähr): G.P. 567,631, Kl 12g, Jan. 6, 1933.
Desulfurization of gases containing CO and $\text{H}_2$ .	Contact mass making the reaction space tight.	Ruhrchemie A.-G.: E.P. 460,017, Feb. 18, 1937.
Desulfurization of a gaseous $\text{N}_2$ - $\text{H}_2$ mixture containing organic S.; T. 298-773°: $\text{CS}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{S}$ space velocity, 1000 at 300°; purification, to 99% (100% purification at 400°); C precipitation not observed.	(1) Porous catalyst consisting of $\text{Al}_2\text{O}_3$ , CaO, $\text{SiO}_2$ , $\text{TiO}_2$ (2) 24% bauxite (3) 35% bauxite (best action)	Awdejewa and Ljudkowskaja: <i>Zhur. Khim. Prom. (U.S.S.R.)</i> , 14, 824-831 (1937).
Purification of gases; removal of S from $\text{SO}_2$ containing dry gas in contact with catalyst; T. greater than 400°.	Porous lime, glass, asbestos, or the like.	Beckman: U.S.P. 2,090,828, Aug. 24, 1937.
Desulfurization of distillation gases of brown coal for catalytic purposes; the gas, freed from $\text{H}_2\text{S}$ but still containing $\text{C}_6\text{H}_6$ or benzene hydrocarbons for the purpose of removing these substances and part of the organic S cpds., is led through the active charcoal; thus a part of the CO and the largest part of the organic S cpds. left are converted by means of water vapor into $\text{CO}_2$ and $\text{H}_2$ respectively; $\text{H}_2\text{S}$ and $\text{CO}_2$ removed in known manner; the remaining organically-bound S is then bound by active charcoal.	Active charcoal.	Dietrich: G.P. 671,189, Kl 26d, Feb. 1, 1939.
Desulfurization of gases.	Iron oxide and/or iron hydroxide containing active charcoal.	Brimsdown Chemical Works, Ltd. and Hene: E.P. 498,734, Feb. 9, 1939.



Table 7. Catalytic Purification of Gases; Removal of Carbon Monoxide.

Reaction	Catalyst	Observer
Purification of gases; removal of CO from H <sub>2</sub> .	Zn, Zn—Cr, Zn—Cu.	Lazote, Inc.: E.P. 258,887, Nov. 17, 1926.
Purification of gases; removal of CO from motor gas waste at 200–500°; CO reacts with water vapor present in the waste gas to form CO <sub>2</sub> and hydrogenation is accelerated.	An oxide of the 7th group with the addition of Th, Al, K, Ce, Mn and Cr oxides.	McIlraith (Neville): U.S.P. 1,867,325, July 12, 1932.
Purification of gases; removal of CO from combustion gases.	Porous C activated before reaction by treating with CO <sub>2</sub> or water vapor at 500–700°; it may also be impregnated with cpds. of alkalies, alkaline earths, and magnesium.	Bertelsmann (Becker and Witt): Swiss P. 158,191, Jan. 16, 1933.
Purification of gases; removal of CO from combustible gases containing CO; a two-stage process: (1) oxidation with H <sub>2</sub> O vapor whereby the CO content is decreased to 4–5%; (2) reduction with H <sub>2</sub> (hydrogenation) whereby the gases are freed from the remaining CO.	(1) Oxidizing substances, such as Cr <sub>2</sub> O <sub>3</sub> +Fe, with active charcoal as carrier; (2) Ni+ThO <sub>2</sub> with active charcoal as carrier	Remmer: G.P. 617,565, Kl 26a, Aug. 21, 1935.
Purification of gases; removal of CO from gases obtained in combustion engines.	Noble metals, such as Pd, precipitated on carriers; metals obtained by oxidation at high temp. or by heating of an oxide layer; as carriers may serve such resistant metal cpds. as special steels containing Al, Cr, Ni, or the like, e.g., "microtherm," "Sicromal."	Degea A.-G. (Auergesellschaft): F.P. 814,695, June 28, 1937.

Table 8. Catalytic Purification of Gases and Liquids.

Reaction	Catalyst	Observer
Purification of gases.	Contact mass.	Nitrogen, G.m.b.H.: G.P. 312,726, Kl 12g, Gr 2, March 16, 1919.
Purification of crude gases with water vapor; removal of CO from CO <sub>2</sub> after or before the application of the hydrogenation gas.		Bergius: G.P. 435,588, Kl 12i, Gr 1, Oct. 13, 1926.
Purification of gaseous mixtures; the gas is brought into contact with the catalyst by a direct electric discharge.	Usual catalysts.	Metallurgic Soc.: F.P. 644,181, Oct. 3, 1928.
Purification of gases; removal of gaseous catalyst poisons from rust gases.		Metall A.-G. (Lechler): G.P. 489,071, Kl 12i, Jan. 13, 1930.
Purification of gases; preparation of pure N <sub>2</sub> .		Harteck: <i>Ber.</i> , 63, 427–429 (1930).
Purification of gases; a mixture of hydrocarbons in vapor state refined at 200–300° in the presence of water vapor, a stream of H <sub>2</sub> and vapors of C <sub>4</sub> H <sub>4</sub> .	Metal catalyst obtained by reduction of oxides of the Fe group contained in minerals and vapors of hydrocarbons; bauxite reduced at 400–450° in an iron tube.	Deutsche Petroleum A.-G. (Riesenfeld, Philippovitch and Bandte): G.P. 501,691, Kl 23b, July 15, 1930.
Purification of gases; direct preparation of pure gases (compressors and pumps used in the equipment).		Pattart: <i>Oesterr. Chem.-Ztg.</i> , 34, 188–190 (1931).
Purification of gases for the catalytic preparation of C under pressure; S adsorbed in the purification process does not interfere, since it has not been regenerated; C-containing product obtained from gases rich in CO with Fe catalyst.	Mixture of powdered C and Fe.	General Carbonaphtha Co.: F.P. 729,460, July 25, 1932.

Table 8 (Continued).

Reaction	Catalyst	Observer
Purification of H <sub>2</sub> -containing gases under pressure.		I. G. Farbenindustrie A.-G.: F.P. 731,308, Sept. 1, 1932.
Purification of fresh H <sub>2</sub> gas in catalytic preparation of NH <sub>3</sub> ; introduced first into a low-pressure area and then into a high-pressure area for improving the degree of purification after compression (between the synthesis apparatus and the ammonia condenser).		Elektrizitätswerke Lanza und Chemische Fabriken A.-G.: Swiss P. 157,025, Nov. 16, 1932.
Purification of gases; removal of combustible materials from exhaust gases of combustion engines by catalytic oxidation; temp. of outlet gases generally sufficient for complete catalytic oxidation.	Cu chromite, (CuO) <sub>2</sub> , Cr <sub>2</sub> O <sub>3</sub> ; catalyst reduced in an oxidizing atmosphere.	Carbon Monoxide Eliminator Corporation (Frazer and Kassel): U.S.P. 1,902,160, March 21, 1933.
Purification of air; air is brought into contact with a mixture of an alkali trioxide and NaOH in the presence of catalyst MnO <sub>2</sub> , setting free O <sub>2</sub> from oxygen trioxide.	MnO <sub>2</sub> .	Dupont (Zisch). U.S.P. 1,922,187, Aug. 15, 1933.
Purification of gases; refining of hydrocarbons, such as benzene, lubricant fractions (750-879°) by hydrogenation under hydrogen pressure; hydrocarbons improved in color; S and tar-ring determined.	Metals of the 6th group.	Standard Oil Development Co. (Jennings): (refer to C 1932 V 103.)
Purification of organic liquids by catalytic reduction of oxides of C which contain instead of or besides methanol also other O-containing or O-free organic cpds.; 100 parts of a fractional distillate (105-100°) obtained by catalytic reduction of oxides of C-containing crude oil distilled with 2 parts slaked lime; 90 parts of water-clear distillate obtained.	Na <sub>2</sub> CO <sub>3</sub> , CaCO <sub>3</sub> , lime; boiling with reflux condenser or distilling over.	I. G. Farbenindustrie A.-G.: G.P. 542,616, KI 120, Jan. 27, 1932.
Purification of crude paraffin, ceresin and Montan wax at 300° and 75 atm. pressure; white paraffin (m.p. 53°) obtained.	Bi, V, or both in the presence of Fe, Ni, or Co, or a mixture of three metals (3rd, 4th and 6th groups); also a catalyst, Bi and Ni on silica gel.	E.P. 367,939, March 24, 1932; add to E.P. 320,921. F.P. 39,860, March 18, 1932.
Purification of gases; vapor-phase refining of gasoline.	Solid H <sub>3</sub> PO <sub>4</sub> .	Ipatieff and Corson: Univ. Oil Prod. Co. (1932).
Purification of gases; refining of hydrocarbon oils; air and O-containing gases conducted through; volatile parts taken away by air from the first receiver; the 2nd and 3rd are partially collected in the condenser; 40-60 hours treatment; petroleum has only a slight odor of terpene.	Gases containing O in the presence of a catalyst; heavy metal salts, such as Pb or Cu filings treated with the fatty, naphthenic or resin acids dissolved in one part of distillate.	Petrow: G.P. 570,564, KI 23b, Feb. 17, 1933.
Purification of N <sub>2</sub> -H <sub>2</sub> mixtures according to the reaction: H <sub>2</sub> +1/2O <sub>2</sub> →H <sub>2</sub> O (freed from O <sub>2</sub> ); T. 125-425°; volume velocity, 15,000-30,000; catalyst works well and the O <sub>2</sub> content is reduced from 1.0% to 0, depending on conditions.	Al-Ni; catalyst prepared by saturating pumice with a solution of Ni(NO <sub>3</sub> ) <sub>2</sub> and Al(NO <sub>3</sub> ) <sub>3</sub> , dried and glowd for the removal of nitrogen oxides; the catalyst contains 9% Ni and 3% Al with respect to pumice.	Awdejewa: <i>Zhur. Khim. Prom.</i> (U.S.S.R.), 14, 637-646 (1937).
Purification of gases; preparation of practically pure CO <sub>2</sub> .	A washing liquid regenerated on heating without mechanical agents; washing follows under 10 atm. pressure.	I. G. Farbenindustrie A.-G.: F.P. 832,585, Sept. 29, 1938.
Purification of gases by two methods with and without removal of CO <sub>2</sub> .		Schuster: <i>Brennstoff-Chem.</i> , 19, 357-359 (1938).

Table 8 (Continued).

Reaction	Catalyst	Observer
Purification of gases (especially distillation gases which were led with $O_2$ over Fe oxide masses); before removal of C oxides, the gases are pretreated, using catalysts to remove $O_2$ ; this treatment with the precontact is instituted between the saturation of the gas with vapor and the catalytic CO conversion.	Cu-containing catalyst.	Brandt: E.P. 490,920, Sept. 22, 1938.
Preparation of CO-free $O_2$ from chlorate or perchlorate-containing masses; $CO$ is oxidized by catalysts to $CO_2$ , which is bound partially or completely by alkali or alkaline-earth oxides, as well as peroxides of the impregnated layer.	Glass wool or pumice powder impregnated with a mixture of Mn oxides with $CuO$ .	I. G. Farbenindustrie A.-G. (Balz and Bloch); U.S.P. 2,143,367, Jan. 10, 1939.

## PART XV

## Catalytic Alkylation in Organic Chemistry

Table 1. Catalytic Alkylation of Paraffinic Hydrocarbons.

Reaction	Catalyst	Observer
Alkylation of paraffinic hydrocarbons with olefins.	Metal halides.	Ipatieff and Pines: U.O.P.
Alkylation of paraffinic hydrocarbons (isobutane) with olefins ( $C_2H_4$ , $C_3H_6$ , $C_4H_8$ ).	$BF_3$ and $Ni-H_2O$ .	Ipatieff and Grosse: <i>J. Am. Chem. Soc.</i> , <b>57</b> , 1616 (1935).
Alkylation of isopentane (75 g.) with ethylene; T. $150^\circ C$ .; maximum pressure, 50 atm.	15.0 g. $BF_3$ 7.5 g. HF 5.0 g. Ni powder.	
Alkylation of paraffinic hydrocarbons with olefins.	$AlCl_3$ .	Ipatieff, Grosse, Pines and Komarewsky: <i>Ibid.</i> , <b>58</b> , 913-915 (1936).
Alkylation of hexane with ethylene; T. $50-60^\circ$ ; ordinary pressure.	$AlCl_3$ .	Ipatieff: "Catalytic Reactions at High Pressures and Temperatures," p. 562, The Macmillan Company, New York, 1936.
Alkylation of $n$ -hexane with ethylene (2.0-2.5 mol $C_2H_4$ reacted with one mol $n$ -hexane); T. $29^\circ C$ .; pressure, 15 atm.	$AlCl_3$ .	Ipatieff, Grosse, Pines and Komarewsky U.O.P.: (unpublished).
Alkylation of propane and butanes with propylene and butylenes; T. $(-50^\circ)$ to $(+75^\circ)$ ; 50 parts of isobutane are cooled to $-30^\circ$ and stirred with 20 parts of the catalyst whereby a cooled stream of isobutylene containing a small amount of HCl is introduced; product obtained has a c.p. below 205 and corresponds in knock stability to a mixture of 85% iso-octane and 15% $n$ -heptane.	$AlCl_3$ or $ZrCl_4$ and HCl.	Universal Oil Products Company: Ipatieff and Pines: F.P. 823,592, Jan. 22, 1938. Ital. P. 351,888, June 5, 1937.
Alkylation of gaseous paraffinic hydrocarbons, e.g., isobutane is alkylated with a mixture of 1, and 2, $n$ -butylene to isooctane; T. $(-50^\circ)$ to $(+10^\circ)$ .	(1) Finely divided Ni. (2) $BF_3$ and HF added under pressure; temp. is kept 4 to 5 hrs. at $0^\circ$ (600 parts introduced in the reaction space).	Universal Oil Products Company: F.P. 823,594, Jan. 22, 1938. Ital. P. 351,890, June 5, 1937.
Alkylation of low-boiling aliphatic hydrocarbons; gasoline with a low anti-knock value is improved by dispersing the catalyst in it and introducing at low temp. a mixture of isobutane and isobutylene, as well as traces of HCl; if $O^\circ$ is used, the products obtained have an octane number of 86.	$AlCl_3$ .	Universal Oil Products Company (Ipatieff and Pines): U.S.P. 2,112,846, April 5, 1938. Universal Oil Products Company: F.P. 823,592, Jan. 22, 1938. F.P. 823,593, Jan. 22, 1938. (Refer to C. 1938 I 4262) U.S.P. 2,112,847, April 5, 1938.

Table 1 (Continued).

Reaction	Catalyst	Observer
Alkylation of isobutane with propylene to isoheptane and 20% isodecane at 0° to (-50°).	AlCl <sub>3</sub> and HCl.	
Alkylation of aliphatic saturated or unsaturated alcohols with 1-20 carbons in the chain by PCl <sub>3</sub> ; T. 20-300°; from the alkyl chlorides through condensation with NH <sub>3</sub> or primary or secondary amines are prepared alkyl amines; T. 140-250°; e.g., 74 g. butyl alcohol are added dropwise to 100 g. PCl <sub>3</sub> within 30 minutes; T. 0-10°; butyl chloride is formed which distills over at 78°.	Metal chlorides.  ZnCl <sub>2</sub> .	Fabryka Chemiczna Wola Krzysztoporska: Polish P. 26,428, June 11, 1938.
Alkylation of 2,2,4-trimethylpentane with various alkyl benzenes and polynuclear aromatic hydrocarbons; T. 90-100°; with naphthalene T. 125-150°; the alkylation reaction may be expressed:	AlCl <sub>3</sub> + HCl.	Grosse, Mavity and Ipatieff: <i>J. Org. Chem.</i> , <b>3</b> , 448-455 (1938).
(1) $\text{ArH} + (\text{CH}_3)_3\text{C}-\text{CH}_2-\text{CH}(\text{CH}_3)_2 \longrightarrow \text{ArC}(\text{CH}_3)_3 + \text{CH}(\text{CH}_3)_3$ Further reaction may lead to the formation of aromatic hydrocarbons with more than one tertiary butyl group in the molecule; in the case of fluorene the hydrogenation-dehydrogenation reaction predominates. (2) $\text{C}_{13}\text{H}_{10} + \text{C}_4\text{H}_{10} \longrightarrow \text{C}_{13}\text{H}_8 + 2\text{C}_4\text{H}_{10}$ The structure of the aromatic hydrocarbon is an important factor.	Catalyst	
Alkylation of metanilic acid (0.702 mol) by C <sub>2</sub> H <sub>5</sub> Cl (2.867 mol) in an aqueous or aqueous alcoholic medium in which side reactions with formation of alcohol and ether take place; 9.5% ethyl chloride does not react; 47.4% used for the ethylation of metanilic acid and 43% for side reactions, whereby 56% forms ether and 44% ethyl alcohol; the ether formed from sodium ethylate cannot be used in the interpretation of the reaction mechanism because, under certain conditions, the reaction: $\text{C}_2\text{H}_5\text{Cl} + \text{C}_2\text{H}_5\text{OH} + \text{NaOH} \longrightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{H}_2\text{O} + \text{NaCl}$ makes it stop practically on the left side; intermediate formation of oxonium compounds is assumed as the mechanism of the reaction similar to that of Hofmann's reaction in amide disintegration; olefin formation from alkyl halides with alcoholic K, as well as the conversion of ether in ethyl sulfate by HSO <sub>3</sub> Cl are interpreted according to the same theory.	Aqueous alcoholic NaOH—Na <sub>2</sub> CO <sub>3</sub> solution.	Ismailski and Popoff: <i>Zhur. Obshchei Khim.</i> (U.S.S.R.) (69), 111-117 (1937).

Table 2. Catalytic Alkylation of Naphthenes.

Reaction	Catalyst	Observer
Alkylation of naphthenes: methyl cyclohexane and methyl isopropylcyclohexane.	AlCl <sub>3</sub> .	Ipatieff and Komarewsky: U.O.P. (1932).
Alkylation of naphthenes with olefins.		Ipatieff, Komarewsky and Grosse: <i>Zhur. Obshchei Khim.</i> (U.S.S.R.), <b>6</b> (68), 433-438 (1936).
Alkylation of naphthenes and paraffins with olefins.		Ipatieff and Grosse: <i>Ibid.</i> , <b>6</b> (68), 423-432 (1936).

Table 3. Catalytic Alkylation of Aromatic Hydrocarbons.

Reaction	Catalyst	Observer
Alkylation of aromatic hydrocarbons.	Zr, Th, Be, Ta, Ti; Be and B halides.	Ipatieff and Grosse: U.O.P.
Alkylation of aromatic hydrocarbons: anthraquinone.	Ni salts.	Brauss, Bayer and Fieser: <i>Ann.</i> , <b>459</b> , 287-304 (1927).
Alkylation of aromatic hydrocarbons to lubricating oils consisting of ethyl and diethyl naphthalene; T. 240°C.; pressure, 80-85 atm.; yield, 1300 g. oil.	AlCl <sub>3</sub> (40 g.).	Wulf: <i>Z. angew. Chem.</i> , <b>41</b> , 626 (1928).

Table 3 (Continued).

Reaction	Catalyst	Observer
Alkylation of aromatic hydrocarbons.	Instead of $\text{HF}_3$ , dioxylfluorboric acid $[\text{H}(\text{BF}_2(\text{OH})_2)]$ and/or its $\text{BF}_3$ addition cpds. is used in the preparation described in (Refer to C. 1935 I 3769).	Dupont (Nieuwland and Sowa): E.P. 463,545, April 29, 1937.
Alkylation of cyclic cpds.; aromatic cpds., together with cpds. containing double bonds, such as unsaturated hydrocarbons, ketones, anhydrides; temp., 150–300°; heterocyclic cpds., such as pyridine, quinoline, thiophene, may be alkylated in this manner; lubricating oils, containing cyclic cpds. may be treated by this method to obtain products with better viscosity properties.	Anhydrous $\text{P}_2\text{O}_5$ .	Shell Development Co. (Malishev): U.S.P. 2,141,611, Dec. 27, 1938.
Alkylation of a mixture of polymerized olefins with acids of the formula $\text{RXR}_2\text{COOH}$ ( $\text{R}$ = mono or polynuclear aromatic residue; $\text{R}_1$ = aliphatic residue; $\text{X}$ = hydrogen or sulfur) to prepare nuclear alkylated aromatic cpds.	$\text{BF}_3$ , $\text{AlCl}_3$ .	I. G. Farbenindustrie A.-G.: Belg. P. 423,516, March 14, 1938.

Table 4. Catalytic Alkylation of Benzene.

Reaction	Catalyst	Observer
Alkylation of benzene with alkyl halides.	$\text{AlCl}_3$ .	Friedel and Crafts:
Alkylation of aromatic ring; benzene to ethyl benzene.	Olefins: ethylene; $\text{AlCl}_3$ suspension.	Milligan and Reid: <i>J. Am. Chem. Soc.</i> , <b>44</b> , 206 (1922).
Alkylation of benzene with olefins to mono- and hexaethyl benzene; T. 70–90°C.; stirring rate, 12,000 r.p.m.; 8 volumes ethylene to 1 volume benzene per minute.	$\text{AlCl}_3$ or $\text{AlBr}_3$	Milligan and Reid: <i>J. Am. Chem. Soc.</i> , <b>44</b> , 206 (1922).
Alkylation of benzene with amylene.	$\text{H}_2\text{SO}_4$ .	Ipatieff, Orlov and Petrow: <i>Ber.</i> , <b>60</b> , 1006 (1927).
Alkylation of aromatic hydrocarbons with olefinic hydrocarbons in the preparation of ethyl benzene, propyl benzene, butyl benzene, amyl benzene, acetylene benzene and propyl naphthalene.	$\text{H}_2\text{SO}_4$ .	Ipatieff and Pines: U.O.P.
Alkylation of benzene with ethylene to mono-, di-, tri-, tetra-, penta- and hexaethyl benzene; T. 50–100°.	$\text{ZrCl}_2$ .	Ipatieff and Grosse: U.O.P.
Alkylation of benzene with ethylene.	Ta pentachloride.	Ipatieff: U.O.P.
Alkylation of benzene with olefins.	$\text{H}_2\text{SO}_4$ , $\text{H}_3\text{PO}_4$ .	Ipatieff, Corson and Pines: <i>J. Am. Chem. Soc.</i> , <b>58</b> , 919 (1936).
Alkylation of aromatic hydrocarbons:		Universal Oil Products Company (Ipatieff and Komarewsky):
(1) benzene with paraffinic hydrocarbons, such as ethane; almost no olefins formed with alkylated aromatics;	10% $\text{H}_3\text{PO}_4$ .	(1) U.S.P. 2,098,045 (2) U.S.P. 2,098,046 refer also to
(2) alkylated aromatics prepared from a mixture of naphthenes and paraffinic hydrocarbons, e.g., equal parts of hexane and cyclohexane are heated at 450° for 12 hrs.; T. 350–480°; pres-	5–15% $\text{H}_3\text{PO}_4$ .	Ipatieff, Komarewsky and Pines: <i>Zhur. Obshchei Khim.</i> (U.S.S.R.), <b>6</b> (68), 1525–1527 (1936).

Table 4 (Continued).

Reaction	Catalyst	Observer
sure, 1-100 atm.; yield, 60% alkylated aromatics (b.p. 110-170°) suitable as additions to motor fuels because they increase the anti-knock value.	15% H <sub>3</sub> PO <sub>4</sub> .	
Alkylation of benzene with esters: (1) <i>n</i> - and <i>sec</i> -butyl ester (formate, acetate, phosphate) to <i>sec</i> -butyl benzene; isobutyl formate to <i>tert</i> -butyl benzene; (2) propyl- and isopropyl ester (formate, acetate, trichloracetate, sulfate) to isopropyl benzene; olefins, intermediate products.	AlCl <sub>3</sub> or BF <sub>3</sub> .	McKenna and Sowa: <i>J. Am. Chem. Soc.</i> , <b>59</b> , 1204-1205 (1937).
Alkylation and polymerization of hydrocarbons: (1) benzene and ethylene, using P <sub>2</sub> O <sub>5</sub> on soot and 1% HCl to ethyl benzene; T. 250°; pressure, 30 atm.; (2) benzene with H <sub>2</sub> to a mixture of benzene and cyclohexane; T. 300°; pressure, 100 atm.; (3) isobutene to isoparaffin; T. 250°; 100 atm. H <sub>2</sub> pressure; (4) diisobutylene to butane; T. 400°; 50 atm. H <sub>2</sub> pressure.	P <sub>2</sub> O <sub>5</sub> with activators such as H <sub>2</sub> S, HCl, HBr, HF, HCN, also H <sub>2</sub> O (too much water is injurious).  P <sub>2</sub> O <sub>5</sub> -cresol as activators.  P <sub>2</sub> O <sub>5</sub> -cresol as activators.	Standard Oil Development Co.: F.P. 821,688, Dec. 10, 1937.
Alkylation of: (a) 100 g. benzene with 20.4 g. ethylene to 105.5 g. 5% liquid toluene, and (b) 100 g. cyclohexane with 151 g. ethylene to 5% toluene; T. 350°; reactions assumed: (1) cyclohexane is dehydrogenated to benzene; (2) benzene is alkylated to ethyl benzene; (3) ethyl benzene decomposes into toluene and methane; alkylation of cyclohexane does not take place; cyclohexane alone gives same reaction as benzene and H <sub>2</sub> ; ethylene led over the same catalyst at 300-350° gives no liquid products, only methane and ethane, but no olefins.	Ni-Al; hydrogen catalysts.	Komarewsky: <i>J. Am. Chem. Soc.</i> , <b>59</b> , 2715-2716 (1937).
Alkylation in the preparation of alkyl benzenes from olefinic hydrocarbons obtained in the cracking of benzene and benzene; strong exothermic reaction; reaction starts at once, without an incubation period; T. 35-40°; yield of mono-substitution derivatives, 68%; using paraffins or naphthenes instead of benzene, no reaction takes place with catalyst FeCl <sub>3</sub> , but does occur with catalyst AlCl <sub>3</sub> .	FeCl <sub>3</sub> (anhydrous).	Kuryndin, Wojewodowa and Ras- kasowa: <i>Zhur. Priklad. Khim.</i> (U.S.S.R.), <b>10</b> , 877-881 (1937).
Alkylation of benzene with isopropylethylene (the isopropylethylene is converted into trimethylethylene and this isomerization takes place during alkylation at 0°; because of isomerization, tertiary amyl benzene is obtained instead of 2-methyl-3-phenyl butane because of the displacement of the double bond in olefins under the influence of a catalyst; alkylation of benzene with cycloparaffins, e.g., cyclopropane, as well as methylcyclobutane to <i>n</i> -propylbenzene, also tertiary-amyl benzene; from the formation of the latter it follows that (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OSO <sub>2</sub> OH primarily formed from methylcyclobutane causes a conversion to (CH <sub>3</sub> ) <sub>2</sub> C(C <sub>2</sub> H <sub>5</sub> )OSO <sub>2</sub> OH which induces the alkylation of benzene; likewise benzene may be alkylated with cyclopentane.	96% H <sub>2</sub> SO <sub>4</sub> .	Ipatieff, Pines and Schmerling: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 353-354 (1938).
Alkylation of chlorobenzene with an olefin; NH <sub>3</sub> is permitted to act on the alkylated product, for example, ethylene is led into a mixture of chlorobenzene and AlCl <sub>3</sub> at 80° under pressure for 4 hours; <i>o</i> - and <i>m</i> -ethyl chlorobenzene and 3,5-diethyl chlorobenzene are formed; the mixture consists of <i>o</i> - and <i>m</i> -ethyl chlorobenzene and is heated in a bomb at 225° with conc. NH <sub>3</sub> for 20 hours; a mixture of 20% <i>o</i> -ethyl amine (b.p. 213-215°) and 80% <i>m</i> -ethyl aniline (b.p. 215-217°) is obtained.	AlCl <sub>3</sub> .          CuO.	Dow Chemical Co. (Dreisbach): U.S.P. 2,159,370, May 23, 1939.

Table 5. Catalytic Alkylation of Phenols.

Reaction	Catalyst	Observer
Alkylation of phenols with amy-lene.	H <sub>2</sub> SO <sub>4</sub> .	Königs: <i>Ber.</i> , <b>23</b> , 3145 (1890).
Alkylation of phenols with methyl, ethyl and propyl alcohols to propyl phenol and propyl ether; T. 380-400°; maximum pressure, 125-130 atm.; time, 12 hrs.	Alumina.	Ipatieff: <i>Ber.</i> , <b>37</b> , 2986 (1904). Ipatieff, Orlow and Rasuvaev: <i>Bull. soc. chim.</i> , 157 (1925). Ipatieff, Orlow and Petrow: <i>Ber.</i> , <b>60</b> , 1006 (1927).
Alkylation of phenols with olefins and terpenes.	H <sub>2</sub> PO <sub>4</sub> .	Ipatieff, Pines, Komarewsky and Chichibabin: <i>Bull. soc. chim.</i> , 497 (1935).
Alkylation of phenols; 980 g. phenol+1132 g. 2,4-dimethyl-pentanol-3 heated over a catalyst form <i>p</i> -tert-heptylphenol; T. 150°; time, 7 hrs.; likewise phenol or $\beta$ -naphthol are alkylated with mixtures of higher alcohols obtained by the catalytic preparation of methanol from CO and H <sub>2</sub> .	ZnCl <sub>2</sub> (1080 g.).	Dupont (Brubaker): U.S.P. 2,110,077, March 1, 1938.
Alkylation of phenols followed by preparation of esters; the phenols are alkylated with halogen alkylene and treated with organic acylation agents; e.g., 800 g. chloroparaffin (Cl content, 14%), and 74 g. phenol over the catalyst are heated to 120° then slowly to 175° until HCl development discontinues, then cooled up to 150° and 80 g. of phthalyl chloride gradually are added; phthalic acid ester of the paraffin-substituted phenol is obtained; instead of phenol, <i>p</i> -cresol, resorcinol, $\beta$ -naphthol, or <i>o</i> -oxydiphenyl may be used; instead of phthalyl-chloride, chlorides of acetic, benzoic, stearic, adipinic, or cinnamic acids may be used.	24 g. AlCl <sub>3</sub> .	Socony-Vacuum Oil Co., Inc. (Reiff and Badertscher): E.P. 491,323, Sept. 29, 1938.
Alkylation of phenols; 130 g. <i>o</i> -cresol and 33.6 g. dodecylene form 4, <i>sec</i> -dodecyl- <i>o</i> -cresol; T. 90-95°; likewise, <i>o</i> -cresol and octylene form 4, <i>sec</i> -octyl- <i>o</i> -cresol.	Salts of HClO <sub>4</sub> : 7.5 g. Al(ClO <sub>4</sub> ) <sub>3</sub> water content, 43%). Fe(ClO <sub>4</sub> ) <sub>3</sub> (water content, 29%) may be used alone or in a mixture with 4.2 g. Pb(ClO <sub>4</sub> ) <sub>2</sub> and 2 g. H <sub>2</sub> O.	Henkel & Company, G.m.b.H.: E.P. 484,151, May 26, 1938.
Alkylation; ethylation of phenol proceeds with ease; T. 200°; pressure, 95 atm. with formation of <i>o</i> - and <i>p</i> -ethyl phenol, diethyl phenol and higher ethylated phenol; furthermore, phenetol, <i>o</i> - and <i>p</i> -ethyl phenetol, and higher phenetols; when cyclohexane is used as solvent the yield in alkali-soluble products increases; propene reacts with phenetol in the presence of H <sub>2</sub> PO <sub>4</sub> at 145° with formation of nuclear-alkylated cpds.; from the experiments it follows that the formation of ethers does not represent a necessary intermediate step in the carbon alkylation of phenols.	H <sub>2</sub> PO <sub>4</sub> .	Ipatieff, Pines and Schmerling: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 1161-62 (1938). (Refer to C. 1938 I 1560).
Alkylation of phenols; phenols are treated with high molecular weight olefins in the presence of a large amount of conc. H <sub>2</sub> SO <sub>4</sub> , which in this case, is not only a catalyst, but has a simultaneous sulfonating or esterifying action upon the alkyl phenol, e.g., 282 g. phenol, 663 g. triisobutylene and 306 g. 96% H <sub>2</sub> SO <sub>4</sub> react upon one another at 60° for one hour, then are neutralized with a solution of 260 g. NaOH in 400 g. water; the alkali salts are used as textile agents.	H <sub>2</sub> SO <sub>4</sub> .	Standard Oil Development Co.: U.S.P. 2,162,269, June 13, 1939; refer also to U.S.P. 2,104,412, (Refer to C. 1938 I 3562).

Table 6. Catalytic Alkylation of Naphthalene.

Reaction	Catalyst	Observer
Alkylation of naphthalene; not olefinic, but alkylated benzene is used as a source of propyl groups to form propyl naphthalene.	AlCl <sub>3</sub> .	Berry and Reid: <i>J. Am. Chem. Soc.</i> , <b>49</b> , 3142 (1927).
Alkylation of naphthalene to lubricants; T. 250°.	AlCl <sub>3</sub> .	I. G. Farbenindustrie A.-G.: E.P. 265,601 (1926). E.P. 295,990 (1927). E.P. 323,100 (Dec. 24, 1929). E.P. 326,500 (1930). U.S.P. 1,667,214, April 24, 1928.

Table 6 (Continued).

Reaction	Catalyst	Observer
Alkylation of naphthalene: (1) with ethylene to mono- and diethylnaphthalene; T. 300°C.; (2) with propylene to mono-propylnaphthalene; T. 200°C.	85% $\text{H}_2\text{PO}_4$ .	Ipatieff, Pines and Komarewsky: <i>Ind. Eng. Chem.</i> , <b>28</b> , 222 (1936).
Alkylation of fluorene with propylene to propylfluorene; T. 200°C.	85% $\text{H}_2\text{PO}_4$ .	Ipatieff, Pines and Komarewsky: <i>Ibid.</i> , <b>28</b> , 222 (1936).

Table 7. Catalytic Alkylation of Aromatic Amines.

Reaction	Catalyst	Observer
Alkylation of aromatic amines: preparation of alkyl aniline.	$\text{ThO}_2$ .	Roy: <i>Ind. Eng. Chem.</i> , <b>5</b> , 383-386 (1927).
Alkylation of organic cpds.; propylene converted into esters by the action of carboxylic acids, e.g., benzoic; alcohols to ethers; aliphatic and aromatic amines alkylated with ethylene; alkyl groups introduced into the nucleus of aromatic compounds; naphthalene heated at 250° in an autoclave and subjected to a pressure of 20-40 atms.; ethylene to polyethylnaphthalene derivatives.	Activated silicates obtained by treating bleached earth, clay, kaolin with acids; kaolin heated for several hours up to 100-120° with 25% $\text{H}_2\text{SO}_4$ ; activated tonsil.	Rheinische Kampfer Fabrik A.-G. (Schöllkopf): E.P. 319,205, Nov. 13, 1929.
Alkylation of aromatic amines under pressure to <i>n</i> -alkylated amine.	Activated bleaching earth.	Rheinische Kampfer Fabrik A.-G. (Schöllkopf): F.P. 681,049 (1930).
Alkylation of aromatic amines: 94 parts aniline + 80 parts cyclohexene to <i>n</i> -cyclohexyl aniline; T. 230-240°.	30 parts active bleaching earth.	I. G. Farbenindustrie A.-G.: F.P. 765,450 (1934). E.P. 414, 574 (1934).
Alkylation of aniline; T. 350 and 375°; yield: 45.1% monomethylaniline 59.7% monoethylaniline.	50% $\text{Al}_2\text{O}_3$ + 50% $\text{Fe}_2\text{O}_3$ . 30% $\text{Al}_2\text{O}_3$ + 70% $\text{Fe}_2\text{O}_3$ .	Schuilin, Bitkova and Jermilina: <i>Zhur. Obschies Khim.</i> (U.S.S.R.), <b>6</b> (68), 774-779 (1936).
Alkylation of amines (normal); vapors of aromatic amines are passed, together with vapors of alcohols or ethers (dimethyl ether or ethyl ether); T. 220-250°; depending on the amount or ratio of the components, mono-, and dimethyl-, as well as mono-, and diethyl aniline or toluidine are obtained.	Freshly precipitated $\text{Al}(\text{OH})_3$ .	I. G. Farbenindustrie A.-G.: F.P. 843,843, July 11, 1939.
Alkylation of aromatic hydrocarbons and their halogen derivatives, the former with ethylene hydrocarbons and the latter with the halogen derivatives of these hydrocarbons.	$\text{H}_2\text{SO}_4$ .	Truffault: <i>Bull. soc. chim.</i> , (5), <b>6</b> , 726-36 (1939).

Table 8. Catalytic Alkylation of Chlorides, Phosphates and Sulfides.

Reaction	Catalyst	Observer
Alkylation; monochlorides ( $\text{C}_2\text{H}_5\text{Cl}$ , $\text{C}_4\text{H}_9\text{Cl}$ ) obtained from corresponding olefins or olefin mixtures.	Halide compounds of Bi.	Dow Chemical Co. (Reilly): U.S.P. 2,031,228, Feb. 18, 1936.
Alkylation; alkyl phosphates obtained from gaseous olefins or olefin mixtures and $\text{H}_2\text{PO}_4$ .	$\text{H}_2\text{SO}_4$ .	Universal Oil Products Company (Ipatieff): U.S.P. 2,062,312, Dec. 1, 1936.
Alkylation; preparation of alkylene sulfides, ethylene oxide, propylene oxide with exchange of O for S in the corresponding sulfides.	Alkali chlorides or carbonates.	I. G. Farbenindustrie A.-G.: F.P. 797,621, May 1, 1936.
Alkylation reactions.	Dialkyl and mixed ether, preferable to an alkyl halide (intermediate formation of an alkyl chloride).	Stadnikov and Goldfarb: <i>Ber.</i> , <b>61</b> , 2341 (1928).
Alkylation reactions.	Alcohols.	Huston and Houk: <i>J. Am. Chem. Soc.</i> , <b>54</b> , 1506 (1932). Huston and Strickler: <i>Ibid.</i> , <b>55</b> , 4317 (1933). Huston and Goodemoot: <i>Ibid.</i> <b>56</b> , 2432 (1934).





Table 1 (Continued).

Reaction	Catalyst	Observer
Condensation of chlorinated "Kogasin" with aromatic hydrocarbons to 3 types of lubricating oils, viz.: (1) from 2 mol chloroparaffin, high $H_2$ content (3.5-14.0%), high viscosity index, relatively high pour point; (2) from 1 mol chloroparaffin with several aromatic rings, low $H_2$ content (less than 12.0%), low viscosity index; (3) from several molecules chloroparaffin with aromatic nuclei; hydrocarbon oils of intermediate properties are produced.	$AlCl_3$ .	Koch and Ibing: <i>Brennstoff-Chem.</i> , <b>16</b> , 261 (1935).
Condensation of 2,3-dichloropentane with double amount of water vapor to 1,3-pentadiene; T. 300°; yield, 48-50%.	$MgCl_2$ containing catalyst.	Tischtschenko: Russ. P. 50,691, March 31, 1937; add to Russ. P. 46,570, Sept. 20, 1935. Tischtschenko: (Refer to C. 1936 II 2796).
Condensation of hexahydro- $\alpha$ -cumaranon with benzene to 2-phenylcyclohexyl acetic acid.	$AlCl_3$ .	Ghosh: <i>Science and Culture</i> , <b>1</b> , 299 (1935).
Condensation of w-oxyundecane acid in chloroform, benzene and Decalin as solvents, to lactones (dilactone) and polyesters; the catalyzed reaction is of the 1st order with respect to w-oxyundecane acid; the non-catalyzed reaction is of the 2nd order with activation energy 11,800 $\pm$ 1,000 cal.	p-Toluene sulfonic acid.	Davies: <i>Trans. Far. Soc.</i> , <b>34</b> , 410-420 (1938).
Condensation of hydrocarbons, such as naphthenic, aromatic, or aliphatic, with paraffins having less than 5 C atoms, especially cyclopropane or cyclobutane (T. below +15°), for example: (1) methylcyclohexane and cyclopropane to methylpropylcyclohexane; T. -10°; yield, 40%; as by-products are obtained 20% methyldipropylcyclohexane; (2) benzene cyclopropane to monopropyl benzene; T. +15°; yield, 50%; little (5%) hexapropylbenzene and 25% dipropylbenzene; (3) isobutane + cyclopropane to 50% heptane and 25% decane; T. -30°.	$AlCl_3$ or $ZrCl_4$ ; likewise HCl.  10% $AlCl_3$ and a little HCl.	Universal Oil Products Co.: F.P. 830,037, July 19, 1938.
Condensation of aromatic hydrocarbons with highly chlorinated paraffins; after completion of condensation, water is added in an amount which does not suffice for a complete decomposition of $AlCl_3$ ; then heat to 250-300° and separate on cooling the lubricating oil formed; instead of water aqueous salts such as $Na_2SO_4 \cdot 10H_2O$ , $CuSO_4 \cdot 5H_2O$ , or $BaCl_2 \cdot 2H_2O$ , may be used whereby the salt amt. is measured so that the water of crystallization is insufficient to decompose $AlCl_3$ ; separation of the catalyst sludge and lubricating oil occurs readily.	$AlCl_3$ .	Imperial Chemical Industries, Ltd.: E.P. 491,522, Sept. 29, 1938.
Condensation of oils with a long-chain halogenated paraffin cpd. (an alkyl or acid cpd.); temp. less than the decomposition point of the oil, possibly in the absence of $O_2$ ; presence of HCl gives better color and better yields; the oil obtained has better oxidation stability, lubricating property and improved viscosity index; the lubricating oil may be decomposed, by means of a selective solvent, into paraffin-poor and paraffin-rich parts, and the first, less valuable, may be improved.	$AlCl_3$ , $ZnCl_2$ , or $BF_3$ .	Standard Oil Development Co.: F.P. 827,165, April 20, 1938.

Table 2. Catalytic Condensation of Unsaturated Hydrocarbons (Ethylene).

Reaction	Catalyst	Observer
Condensation of ethylene.	Anhydrous chlorides.	Chem. Fabrik auf Antien (vorm. Schering): G.P. 278,486, Kl 12o Gr 19, May 24 (1913).
Condensation of ethylene with $\text{NH}_3$ to pyridine bases containing condensate; preparation of amines and heterocyclic bases.	$\text{Al}_2\text{O}_3$ . Kaolin, or other silicates.	Tschitschibabin: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>47</b> , 703 (1915). Rheinische Kampfer Fabrik (Schöllkopf): G.P. 638,756 (1937). E.P. 319,205 (1929). F.P. 681,049 (1930).
Condensation of ethylene and other hydrocarbons to condensation products (industrial process).	$\text{BF}_3$ .	Hofmann and Otto: F.P. 632,768 (1927). Hofmann and Wulff: E.P. 307,802 (1929). Otto: <i>Brennstoff-Chem.</i> , <b>8</b> , 321 (1927).
Condensation of ethylene with $\text{CO}_2$ to acrylic acid.	Acid salts; acid metal oxides; salts of $\text{H}_2\text{PO}_4$ , etc., on silicic acid gel or clay pieces.	Röhm-Haas A.-G.: G.P. 553,179 (1932).
Condensation of acetic acid (benzoic acid) with ethylene; T. 500°; 50 atm. pressure; to ethyl acetate or to ethyl benzene.	Au chloride dispersed on active charcoal.	I. G. Farbenindustrie A.-G.: F.P. 774,342 (1934). F.P. 710,846 (1931).
Condensation of acetic acid with ethylene, propylene, butylene, anhydrous amylene; T. less than 300°—about 150°; under pressure to esters.		Standard Oil Development Co. (Frolich and Brezinski): U.S.P. 1,951,747 (1934).
Condensation of unsaturated hydrocarbons, e.g., ethylene at 20–40 atm. pressure with naphthalene forming its homologs.	Active silicates.	Rheinische Kampfer Fabrik: B.P. 319,205, Oct. 9, 1930.
Condensation of ethylene with naphthalene, tetrahydronaphthalene and coal-tar fractions to lubricating oils; the condensation with aromatics is rendered complex by direct polymerization of olefins.	$\text{AlCl}_3$ .	Schilwächter: <i>Angew. Chem.</i> , <b>47</b> 677 (1934).
Condensation of ethylene with aromatic or alicyclic aromatic hydrocarbons.	Aqueous perchloric acid.	Deutsche Hydrierwerke A.-G.: Beig. P. 412,931, May 28, 1936.
Condensation of ethylene with cracking benzine to high molecular weight hydrocarbons.	$\text{H}_2\text{PO}_4$ on kieselguhr.	Peters and Winzer: <i>Brennstoff-Chem.</i> , <b>17</b> , 301 (1936).
Condensation of ethylene at ordinary pressure; T. 700–950°; 100 l./hr.; to benzene, toluene, naphthalene and anthracene.	Silica gel.	Pichler: <i>Ges. Abhandl. Kenntnis Kohle</i> , <b>12</b> , 310–312 (1937).

Table 3. Catalytic Condensation of Olefins with Hydrogen Sulfide.

Reaction	Catalyst	Observer
Condensation of olefins with $\text{H}_2\text{S}$ ; T. 650–725°; to mercaptans, dialkylsulfides and thiophene.	Silicic acid gel.	Maihle and Renandie: <i>Compt. rend.</i> , <b>195</b> , 391 (1932).
Condensation of olefins with $\text{H}_2\text{S}$ ; T. 250°; 22% conversion.	$\text{Al}_2\text{O}_3$ , bentonite, kieselguhr charged with Ni or $\text{H}_2\text{PO}_4$ precipitated on charcoal.	Duffey, Snow and Keyes: <i>Ind. Eng. Chem.</i> , <b>26</b> , 91 (1934).

Table 4. Catalytic Condensation of Olefins with Various Compounds.

Reaction	Catalyst	Observer
Condensation of olefins with aliphatic cpds. having a double bond.	Highly porous hydrosilicates, such as natural bleaching earth.	I. G. Farbenindustrie A.-G.: E.P. 316,951 (1929).
Condensation of unsaturated hydrocarbons to condensation products.	$\text{BF}_3$ .	Hofmann and Wulff: E.P. 307,802 (1929).
Condensation of diolefins: butadiene with $\text{NH}_3$ to organic bases.	$\text{Al}_2\text{O}_3$ , bauxite.	I.G. Farbenindustrie A.-G.: (Schmidt, Fries and Kollek): G.P. 528,466 (1931).

Table 4 (Continued).

Reaction	Catalyst	Observer
Condensation of olefins with paraffinic and naphthenic hydrocarbons.		Ipatieff: <i>J. Am. Chem. Soc.</i> , <b>57</b> , 1616, 1722 (1935).
Condensation of paraffins and cycloparaffins with olefinic hydrocarbons.	AlCl <sub>3</sub> .	Ipatieff and Pines: Unpublished U.O.P.
Condensation of unsaturated hydrocarbons.	AlCl <sub>3</sub> , ZnCl <sub>2</sub> , FeCl <sub>3</sub> (2-10% H <sub>2</sub> O acts as promoter).	N. V. de Bataafsche Petroleum Maatschappij: F.P. 816,663, Aug. 13, 1937.

Table 5. Catalytic Condensation of Olefins with Aromatic Hydrocarbons.

Reaction	Catalyst	Observer
Condensation of olefins with aromatic hydrocarbons either in vapor or liquid phase under normal or increased pressure.	AlCl <sub>3</sub> or BF <sub>3</sub> . H <sub>3</sub> PO <sub>4</sub> . H <sub>2</sub> SO <sub>4</sub> .	Ipatieff: "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Company, New York, 1936. Brochet: <i>Compt. rend.</i> , <b>117</b> , 115 (1893).
Condensation of olefins with more than 3 C atoms with phenols.	Active or natural bleaching earth or other highly porous silicates.	I. G. Farbenindustrie A.-G.: E.P. 316,951 (1929).
Condensation of olefins with Edeleanu extract as aromatic component.	AlCl <sub>3</sub> .	Michel: G.P. 516,653 (1928). B.P. 310,274 (1929). B.P. 310,951 (1929).
Condensation of olefinic gases with aromatic hydrocarbons.	Suspension of AlCl <sub>3</sub> in middle oils.	Krauch: Proc. Intern. Conf. Bituminous Coal, <b>1</b> , 39 (1928). B.P. 299,086 (1929). B.P. 362,465 (1930). F.P. 650,799 (1929). U.S.P. 1,914,727 (1929). U.S.P. 1,965,952 (1934).
Condensation of aromatic hydrocarbons, such as benzene with olefins to unsaturated cyclic hydrocarbons, such as cyclohexane, styrene with olefins.	Hydrosilicates. Activated silicates treated with acids to silicic acid hydrates.	I. G. Farbenindustrie A.-G.: E.P. 316,951 (1929).
Condensation of propylene with <i>m</i> -cresol; nucleus-propylated cresol; T. less than 400°; to thymol.	Al <sub>2</sub> O <sub>3</sub> , chemically-active bleaching earth, silicic acid gel or kieselguhr.	Rheinische Kampfer Fabrik (Schollkopf): G.P. 586,160 (1933). G.P. 638,756 (1929). E.P. 298,600 (1928). E.P. 325,856 (1929). E.P. 319,205 (1929). F.P. 681,049 (1930).
Condensation of olefinic hydrocarbons with aromatic hydrocarbons, e.g., propylene with benzene.	P <sub>2</sub> O <sub>5</sub> .	Truffault: <i>Compt. rend.</i> , <b>200</b> , 406-408 (1935).
Condensation of olefins with benzene, naphthalene, anthracene; T. 150-300°; 50 atm. pressure.	P <sub>2</sub> O <sub>5</sub> dispersed on active substances, such as fuller's earth or silica.	N. V. de Bataafsche Petroleum Maatschappij: E.P. 437,072 (1935). F.P. 782,194 (1935).
Condensation of olefins occurring in cracking benzene with aromatics to alkyl benzenes.	AlCl <sub>3</sub> or ZnCl <sub>2</sub> precipitated on bentonite or fuller's earth.	Universal Oil Products Co. (Egloff): U.S.P. 2,009,108 (1935).
Condensation of olefins with hydroaromatic or heterocyclic cpds. to O <sub>2</sub> -containing organic cpds.	H <sub>3</sub> PO <sub>4</sub> + kieselguhr or silicic acid mixed catalysts.	Universal Oil Products Co. (Ipatieff): U.S.P. 2,018,065 (1935).
Condensation of aromatic hydrocarbons with olefins; T. 180-300°; benzene + isopropylene to isopropyl benzene.	Silicic acid or kieselguhr on which H <sub>3</sub> PO <sub>4</sub> is precipitated.	Universal Oil Products Co. (Ipatieff): U.S.P. 2,018,065 (1935).
Condensation of propylene with 2 mols benzene to mono-, di- and tri-isopropyl benzene.	80 g. H <sub>2</sub> SO <sub>4</sub> with addition of 10 g. BF <sub>3</sub> .	Wunderly, Sowa and Nieuwland: <i>J. Am. Chem. Soc.</i> , <b>58</b> , 1007-1009 (1936).

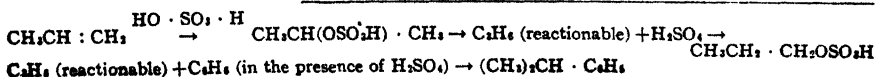


Table 5 (Continued).

Reaction	Catalyst	Observer
Condensation of olefins with aromatic and alicyclic aromatic cpds.; 92 parts toluene + 15.7% catalyst + 23% isobutylene; T. 95-100°; a tertiary butyl group and 2-butyl group are obtained at T. 182-205°.	Aqueous solution of $\text{HClO}_4$ ; likewise together with a solution of $\text{H}_2\text{SO}_4$ , $\text{CH}_3\text{COOH}$ , $\text{H}_3\text{PO}_4$ .	Deutsche Hydrierwerke A.-G.: F.P. 809,128, Feb. 24, 1937.
Condensation of aromatic hydrocarbons with cyclic olefins and terpenes: (1) benzene to cyclohexene; (2) benzene to limonene.	$\text{H}_2\text{SO}_4$ .	Ipatieff and Pines U.O.P.: Unpublished.
Condensation of olefins with aromatic hydrocarbons; to prepare alkylated aromatic hydrocarbons, aromatics are treated with olefins having 3-5 C atoms in ratio at least 2:1 at 0-25°, preferably under 10°, in the presence of the catalyst; the acid separated from the reaction product is used with addition of fresh acid as a condensation catalyst; high yields in alkylated aromatics are obtained without sulfonation as a side reaction.	$\text{H}_2\text{SO}_4$ .	Stanley, Minkoff and Youell: U.S.P. 2,143,493, Jan. 10, 1939.

Table 6. Catalytic Condensation of Acetylene with Water.

Reaction	Catalyst	Observer
Condensation of $\text{C}_2\text{H}_2$ with $\text{H}_2\text{O}$ to (1) furan, or to (2) acetaldehyde, as well as acetic acid. (1) T. 400-425°.	(1) $\text{Al}_2\text{O}_3$ . (2) $\text{HgO}$ dispersed in $\text{H}_2\text{SO}_4$ ; hydration catalyst on active substance.	Tschitschibabin: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>47</b> , 703 (1915). Kutscherow: <i>Ber.</i> , <b>14</b> , 1540 (1881). Erdmann and Köthner: <i>Z. anorg. Chem.</i> , <b>18</b> , 48 (1898).
Condensation of $\text{C}_2\text{H}_2$ ; T. not above 400°.	Activated shell charcoal charged with 1% $\text{HgO}$ or other Hg cpds. or oxides of Zn, Cu, Mo, Fe, Ni, Al.	Bender: U.S.P. 1,355,299 (1920).
Condensation of $\text{C}_2\text{H}_2$ with $\text{H}_2\text{O}$ to acetaldehyde; yield, 65%.	Hydrated Al oxides.	Deutsche Gold- und Silberscheideanstalt: G.P. 365,285 (1922). G.P. 369,515 (1923). G.P. 379,596 (1923).
Condensation of $\text{C}_2\text{H}_2$ or $\text{C}_2\text{H}_4$ -containing gases (25.6%) in the presence of $\text{H}_2$ (74.4%); T. 220-230°; to acetaldehyde and 30-40% $\text{CH}_3\text{COOH}$ of the 66.5% of applied $\text{C}_2\text{H}_2$ .	Salts of Hg, Ag, Sn, or Cu in mixture with silicic acid.	I. G. Farbenindustrie A.-G.: F.P. 644,967 (1929). I. G. Farbenindustrie A.-G.: (Jochheim): G.P. 533,466 (1931).
Condensation of $\text{C}_2\text{H}_2$ with $\text{H}_2\text{O}$ vapor to 90% acetaldehyde.	Oxides, sulfides of Zn or Cd or their mixture with chromates, tungstates or molybdates plus activator $\text{Al}_2\text{O}_3$ .	I. G. Farbenindustrie A.-G.: E.P. 332,635 (1930).
Condensation of $\text{C}_2\text{H}_2$ with $\text{H}_2\text{O}$ vapor and 10% $\text{O}_2$ in the presence of Hg vapor; T. 260°; to 30% acetaldehyde + 45% acetic.	Active charcoal or 8 g. $\text{Al}_2\text{O}_3$ having precipitated on it 11 g. $\text{HgO}$ cpds. + 10 cc. 6% $\text{H}_3\text{PO}_4$ .	I. G. Farbenindustrie A.-G. (Eberhardt): G.P. 544,691 (1931). E.P. 321,241 (1929).
Condensation of $\text{C}_2\text{H}_2$ with $\text{H}_2\text{O}$ .	Fuller's earth, clay or kieselguhr with precipitated oxides and hydroxides of Cu, Mn, V, Ti, Cr; may contain Fe cpds. and hydrated Al silicate; $\text{Al}_2\text{O}_3$ activated by dehydrogenating additions, such as oxides, sulfides, selenides of the 1st or 8th group.	I. G. Farbenindustrie A.-G. (Steuer and Grab): G.P. 504,862 (1931). G.P. 514,591 (1931). F.P. 688,047 (1930).

Table 7. Catalytic Condensation of Acetylene with Hydrogen Sulfide and Hydrogen Cyanide.

Reaction	Catalyst	Observer
Condensation of $C_2H_2$ and $H_2S$ to thiophene and a small amount of thiophene homolog ethyl thiophene (the presence of $O_2$ is favorable).	$Al_2O_3$ , fuller's earth, clay, bauxite, or $Al_2O_3$ with water of hydration.	Tschitschibabin: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>47</b> , 703 (1915). Rhenania Verein Chemische Fabriken (Stuber and Grob): <i>G.P.</i> 367,595 (1922).
Preparation of mono-ethyl amino piperidine, pyridine hydrogenated quinoline; a mixture of $C_2H_2$ and $H_2O$ vapor is condensed at 250–500° with $NH_3$ or amines over catalysts (metals or their oxides); the condensation product is then hydrogenated over Ni; in place of $C_2H_2$ , a $H_2O$ mixture may be used, also the aliphatic or cyclic aldehydes are obtained as intermediate products.	Metals or their oxides; Ni.	I. G. Farbenindustrie A.-G. (Schlecht and Roetger): <i>U.S.P.</i> 1,894,792, Jan. 17, 1933.
Condensation of $C_2H_2$ and $H_2S$ in the presence of liquid solvents, e.g., $H_2O$ to $\alpha$ -trithioaldehyde; T. 101°F.; 10–20 atm. pressure $C_2H_2$ , 12 hrs.; as solvents may be used water, dioxane, mono-, di-, triethylene glycol, propylene glycol, trimethylene-glycol, 1,3-butylene-glycol, glycerol, polyglycerol; condensation products may be ethyl mercaptan, vinyl ethyl sulfide and ethane dithioldiethylether.	Sulfides and polysulfides of alkalis, alkaline earths, $NH_3$ and heavy metals.	I. G. Farbenindustrie A.-G. (Reppe and Nicolai): <i>G.P.</i> 625,660, Kl 120, Feb. 20, 1936.
Condensation of $HCN$ with $C_2H_2$ to vinyl cyanide; T. 400–500°; yield, 10% of the theoretical.	10% $BaCN_2$ on charcoal (heated at 200–300° in a $N_2$ stream).	Konsortium für Elektrochemische Industrie (Baum and Herrmann): <i>G.P.</i> 559,734 (1932).

Table 8. Catalytic Condensation of Acetylene with Ammonia.

Reaction	Catalyst	Observer
Condensation of $C_2H_2$ with $NH_3$ $C_2H_2 + NH_3 \rightarrow CH_3CN + H_2$ (industrial process)	Fe ore, bauxite, permutite.	Rhenania Verein Chemische Fabriken: <i>G.P.</i> 365,432 (1913). <i>G.P.</i> 367,538 (1918).
Condensation of $C_2H_2$ with $NH_3$ $C_2H_2 + NH_3 \rightarrow CH_3CN + H_2$	$ThO_2$ , $ZrO_2$ .	Tschitschibabin: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>47</b> , 709 (1915); <b>54</b> , 611 (1922); <i>J. prakt. Chem.</i> , <b>107</b> , 109 (1924).
Condensation of $C_2H_2$ with $NH_3$ $2C_2H_2 + NH_3 \rightarrow C_4H_5N + H_2$ $3C_2H_2 + NH_3 \rightarrow C_6H_7N + H_2$ $4C_2H_2 + NH_3 \rightarrow C_8H_{11}N$ T. 400–425°; the liquid condensate contains $\alpha$ -picoline, $\gamma$ -picoline, $\beta$ -collidine, collidine.	$Al_2O_3$ , kaolin.	Tschitschibabin: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>47</b> , 703 (1915). Tschitschibabin and Moschkin: <i>Ibid.</i> , <b>54</b> , 611 (1922).
Condensation of $C_2H_2$ with $NH_3$ to acetonitrile; T. 400° in the presence of $H_2O$ vapor.	Bauxite; $Fe(OH)_2$ and $Al(OH)_3$ precipitated from their salts.	Rhenania Verein Chemische Fabriken (Steuer and Grob): <i>G.P.</i> 382,091 (1932); refer also to <i>G.P.</i> 365,432 (1923) and <i>G.P.</i> 369,371 (1923).
Condensation of $C_2H_2$ with $NH_3$ $C_2H_2 + NH_3 \rightarrow CH_3CN + H_2$	$ThO_2$ , $ZrO_2$ .	I. G. Farbenindustrie A.-G.: <i>G.P.</i> 477,049 (1927).
Condensation of $C_2H_2$ with $NH_3$ $C_2H_2 + NH_3 \rightarrow CH_3CN + H_2$	Mud ore, bauxite, permutite, $ThO_2$ , $ZrO_2$ .	Rhenania Verein Chemische Fabriken: <i>G.P.</i> 367,538 (1918). I. G. Farbenindustrie A.-G.: <i>G.P.</i> 477,049 (1927).
Condensation of $C_2H_2$ with $NH_3$ to obtain N-containing products.	Contact masses: hydrated oxides of Fe, Co, or V, especially $V_2O_5$ .	Rhenania Verein Chemische Fabriken: <i>G.P.</i> 467,220, Kl 120, Dec. 28, 1928.

Table 8 (Continued).

Reaction	Catalyst	Observer
Condensation of $C_2H_2$ with $NH_3$ to acetonitrile (75%); 4 parts $C_2H_2$ and 3 parts $NH_3$ .	Al gel + active silicic acid (active silicic acid impregnated with aqueous solution of Zn and Th nitrate).	I. G. Farbenindustrie A.-G.: G.P. 477,049 (1923).
Condensation of $C_2H_2$ with $NH_3$ in the presence of $H_2O$ vapor to excess of pyridine bases; T. $400^\circ$ ; 75% pyridine bases.	$ZnSO_4$ or metals or metal compounds charged on silica gel.	I. G. Farbenindustrie A.-G.: G.P. 685,566 (1930).
Condensation of $C_2H_2$ with $NH_3$ ; gaseous mixture led over catalysts at an increased temp. so that no pyridine bases are formed; amines or acid nitriles result.	Elements of the 2nd or 7th group of the Periodic System.	I. G. Farbenindustrie A.-G.: Belg. P. 366,696, July 17, 1930.
Condensation of $C_2H_2$ with $NH_3$ ; T. $400^\circ$ ; resulting nitrile saponified, giving $(NH_4)_2SO_4$ and AcOH.	$SiO_2$ and anhydrous $ZnCl_2$ .	I. G. Farbenindustrie A.-G.: G.P. 560,543, Oct. 4, 1930.
Condensation of $C_2H_2$ with $NH_3$ to oily liquid organic bases; ratio 1 : 1; yield 55% pyridine homologs.	Cu, Hg, Zn, Cd, Co, Fe as salts of HCN, formic acid, acetic and trichloroacetic acid on porous substances such as coke, diatomite, silica gel, diatomite charged with Fe rodamide.	I. G. Farbenindustrie A.-G. (Nicodemus): G.P. 504,238 (1930). I. G. Farbenindustrie A.-G. (Nicodemus and Schmidt): G.P. 516,765 (1930).
Condensation of $C_2H_2$ with $NH_3$ to acetonitrile (small formation of pyridine bases); T. $300-450^\circ$ .	Metal silicates, metal oxides and hydroxides of Zn, Sn and metal sulfides, $Al_2O_3$ , active charcoal.	I. G. Farbenindustrie A.-G. (Nicodemus): G.P. 547,518 (1932); refer also to I. G. Farbenindustrie A.-G. (Rötger): G.P. 526,798 (1931).

Table 9. Catalytic Condensation of Acetylene with Primary or Secondary Amines.

Reaction	Catalyst	Observer
Condensation of $C_2H_2$ with primary amines (better than secondary); T. $300^\circ$ ; a mixture of pyridine derivatives is obtained, e.g., from methylamine and $C_2H_2$ , 25-30% pyridine and 50-60% pyridine homologs.	Salts able to give ammoniates, e.g., pumice and $ZnBr_2$ .	I. G. Farbenindustrie A.-G. (Nicodemus and Schmidt): G.P. 516,765, Kl 12a Gr 1, Sept. 27, 1928; add to G.P. 479,351.
Condensation of $C_2H_2$ with primary or secondary amines; T. $130^\circ$ , 70-80% nitriles.	Ammoniates on active substances or silica gel and $Al_2O_3$ having dehydrating action.	I. G. Farbenindustrie A.-G. (Nicodemus and Schmidt): G.P. 516,765, Kl 12a Gr 1, Sept. 27, 1928; refer also to I. G. Farbenindustrie A.-G. (Rötger): G.P. 528,897 (1931).

Table 10. Catalytic Condensation of Acetylene with Methane, Ethylene, and Acetic Acid.

Reaction	Catalyst	Observer
Condensation of $C_2H_2$ with methane or its homologs to propylene; T. $200-350^\circ$ .	$SiO_2$ , $TiO_2$ , $Al_2O_3$ , Cu salts; Al and Hg salts; Ni, Co, Fe.	Chemische Fabrik Bückau: G.P. 294,794 (1912). Lonza Elektrische Werke: G.P. 407,485 (1922). Konsortium für Elektrochemische Industrie: G.P. 462,251 (1927). LePétrole Synthétique: F.P. 589,931 (1924).
Condensation of $C_2H_2$ with ethylene to butadiene.	Active charcoal, $Al_2O_3$ , Ni on $Al_2O_3$ .	Koslow and Fedossejew: <i>Synthes. Kauchuk (U.S.S.R.)</i> , 3, No. 5, 36 (1934).
Condensation of $C_2H_2$ with $CH_3COOH$ vapor to vinyl ester.	Metal salts of strong $O_2$ -containing acids on silica gel; Hg sulfate on Japanese acid clay.	Deutsche Gold- und Silberscheidanstalt (Walter): G.P. 599,631 (1934). Kuwata and Kato: <i>J. Soc. Chem. Ind. Japan</i> , 39, 127B (1936).

Table 10a. Catalytic Condensation of Acetylene with Alcohols.

Reaction	Catalyst	Observer
Condensation of $C_2H_2$ with alcohols to vinyl ether.	Charcoal, active charcoal, kieselguhr covered with metals, their oxides or salts.	Konsortium für Elektrochemische Industrie (Baum, Deutsch, Herrmann and Mugdan): G.P. 403,784 (1924). E.P. 182,112 (1922). F.P. 553,076 (1923).
Condensation of $C_2H_2$ with vinyl alcohol to form their ether.	Silica gel with the metal salt of strong O <sub>2</sub> -containing acids.	Deutsche Gold- und Silberscheideanstalt (Walter): G.P. 599,631 (1934).
Condensation of $C_2H_2$ with compounds containing a free OH-group.	Alkali oxides, alkali hydroxides or cyanides, alkali zincate, alkali alcoholate or phenolate on active charcoal.	I. G. Farbenindustrie A.-G.: G.P. 639,843 (1937). E.P. 427,036 (1935).
Condensation of organic oxy-groups containing cpds. such as mono- or polyvalent alcohols, phenols, aliphatic alcohols with $C_2H_2$ (I); dimethyl acetal glycerinacetal, as well as a ruby-red, readily crumbling, resin (120-130°) is prepared from phenol and (I) at 110°.	Freshly precipitated $HgSO_4$ at various temp.	Imperial Chemical Industries, Ltd.: U.S.P. 2,136,217, Nov. 8, 1938.

Table 11. Catalytic Condensation of Acetylene with Ether.

Reaction	Catalyst	Observer
Condensation of $C_2H_2$ with cpds. having triple bonds or conjugated double bonds, such as vinyl and divinyl acetylene, as well as $C_2H_2$ itself, in the presence of a solvent, e.g., ether, to a dark resin (the non-polymerized part may be treated with $Cu_2Cl_2$ ); to 156 g. vinyl acetylene and 241 g. chlormethyl ether are added, after 2 hrs., 100 g. water-free ether, 9 g. $BiCl_3$ and 0.5 g. pyrogallol at 5-15°, stirred and after 7 hrs. 4 g. more of the catalyst are added.	Hydrolyzable metal halide such as $BiCl_3$ or halogenated ethers, chlormethyl ether.	Dupont (Dykstra): U.S.P. 2,119,531, June 7, 1938.

Table 11a. Catalytic Condensation of Acetylene with Carbonic Acid.

Reaction	Catalyst	Observer
Condensation of $C_2H_2$ with carbonic acid to the ester of vinyl alcohol.	Charcoal, active charcoal, kieselguhr.	Konsortium für Elektrochemische Industrie: G.P. 403,784 (1924). E.P. 182,112 (1922). F.P. 553,076 (1923).
Condensation of $C_2H_2$ with carbonic acid to 30% vinyl acetate.	Charcoal, active charcoal, silica gel with precipitated Zn or Cd salts, especially their acetates.	Konsortium für Elektrochemische Industrie (Baum, Deutsch and Herrmann): G.P. 485,271 (1930). E.P. 285,095 (1928). F.P. 649,455 (1929). U.S.P. 1,822,525 (1932). Konsortium für Elektrochemische Industrie (Mugdan and Root): G.P. 553,071 (1932).
Condensation of $C_2H_2$ with carbonic acid; T. 250°; pressure, greater than 20 atm.	Silicates or phosphates of difficultly reducible oxides of metals.	I. G. Farbenindustrie A.-G.: F.P. 710,846 (1931).

Table 12. Catalytic Condensation of Acetylene with Aromatic Amines.

Reaction	Catalyst	Observer
Condensation of $C_2H_2$ with aniline to the <i>trans</i> -isomer of the diethylidene cpd.	$HgSO_4$ , $Hg_2SO_4$ and $HgNO_3$ are also good catalysts; $Hg(CN)_2$ is not suitable as a condensing catalyst.	Eckstein: <i>Ann.</i> , 58-59 (1901).
Condensation of $C_2H_2$ with aniline vapors; T. 360-420° to indole and quinoline homologs (methyl quinoline).	$Al_2O_3$ .	Tschitschibabin: <i>J. Russ. Phys.-Chem. Soc.</i> , 47, 703 (1915).



Table 12 (Continued).

Reaction	Catalyst	Observer
Condensation of $C_2H_2$ with aromatic amines to 2-methyl quinaldine ring instead of the indole ring condensation.	Ammoniates precipitated on porous carriers.	I. G. Farbenindustrie A.-G.: G.P. 495,337 (1930). G.P. 504,238 (1931).
Condensation of $C_2H_2$ with aromatic hydrocarbons to lubricating oil.	$AlCl_3$	N. V. de Bataafsche Petroleum Maatschappij: B.P. 441,806 (1936).
Condensation of $C_2H_2$ with aromatic amines, <i>e.g.</i> , aniline; dilution agent, toluene; at room temp. to ethyl aniline, quinaldine and tetrahydroquinaldine.	$Cu_2Cl_2$ and $CuCl_2$ .	Koslow and Fedossejew: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , 6 (68), 250-258 (1936).
Condensation of $C_2H_2$ with aromatic amines, <i>e.g.</i> , aniline	$Cu_2Cl_2$ .	Koslow and Golod: <i>Ibid.</i> , 6 (68) 1089-1091 (1936).
$C_6H_5NH_2 + 2CH \equiv CH \rightarrow \text{quinoline} - CH_3 + H_2$		
<p>to quinaldine plus ethyl aniline to prevent the formation of secondary amines (tetrahydroquinaldine) because <math>H_2</math> formed intermediary, hydrogenates; nitrobenzene is introduced as oxidizing agent; T. 25-30°; time, 12-15 hrs.; yield, 35.5 g. quinaldine and 8 g. tetrahydroquinaldine are obtained from 100 g. aniline, 30 g. <math>Cu_2Cl_2</math>, 45 g. <math>C_2H_2</math> and 50 g. nitrobenzene.</p>		
Condensation of $C_2H_2$ with aromatic amines to $C_{14}H_{11}N_2$ (solid body); T. 80-83° is considered as intermediary mixture of two stereoisomers, diethylidene aniline cpds. giving quinaldine and tetrahydroquinaldine.	5-20% $HgCl_2$ , $HgCl$ and $HgBr_2$ .	Koslow, Dinarburskaja and Rubina: <i>Ibid.</i> , 6 (68), 1349-1351 (1936).
Condensation of $C_2H_2$ with aromatic amines, such as aniline; intermediate product, $C_{14}H_{11}N_2$ ; T. 81°.	$HI_2$ , $HgCl_2$ and $HgBr_2$ .	Koslow and Patschankowa: <i>Ibid.</i> , 6 (68), 1352-1354 (1936).
Condensation of $C_2H_2$ with aromatic amines, <i>e.g.</i> , $C_2H_5$ with aniline; the condensation product decomposes on heating to quinaldine; yield considerably increased on addition of $ZnCl_2$ ; likewise monoethylidene aniline is formed in addition to quinaldine; the origin of monoethylidene aniline is explained by a depolymerization process.	$HgCl_2$ (two intermediate products isolated).	Koslow and Sserko: <i>Ibid.</i> , 7 (69), 832-835 (1937); <i>Ibid.</i> , 7 (69) 836-838 (1937).

Table 13. Catalytic Condensation of Acetylene with Aromatic Hydrocarbons.

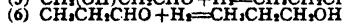
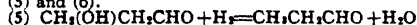
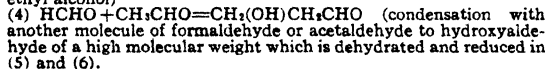
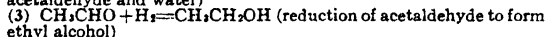
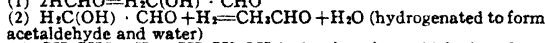
Reaction	Catalyst	Observer
Condensation of $C_2H_2$ to condensation products, <i>e.g.</i> , olefins, aromatics, or cuprene (industrial process).	$SiO_2$ , $TiO_2$ , $Al_2O_3$ , etc. $Cu$ salts.	Chemische Fabrik Bückau: G.P. 294,794 (1912). Lonza Elektrische Werke G.P. 407,485 (1922). Wenzke and Nieuwland: <i>J. Am. Chem. Soc.</i> , 46, 177-181 (1924). Konsortium für Elektrochemische Industrie: G.P. 462,651 (1927). LePétrole Synthétique: F.P. 589,831 (1924). Zelinsky: <i>Ber.</i> , 57, 264 (1924). Zelinsky: <i>Compt. rend.</i> , 177, 182 (1924). Bahr: <i>Abhandlung Kohle</i> , 8, 283 (1929).
	$Al$ , $Hg$ salts.	
	$Ni$ , $Co$ , $Fe$ .	
Condensation of $C_2H_2$ with alcohol or phenol.	One or more difficultly reducible metal oxides or phosphates as well as silicates mixed with at least one heavy metal oxide readily reducible on kieselguhr, active charcoal, or silica gel.	I. G. Farbenindustrie A.-G.: F.P. 710,846 (1931).

Table 13 (Continued).

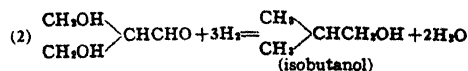
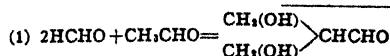
Reaction	Catalyst	Observer
Condensation of $C_2H_2$ with aromatic hydrocarbons to alkylated aromatic hydrocarbons; T. 150-300°; 50 atm. pressure.	Fuller's earth or silica gel.	N. V. de Bataafsche Petroleum Maatschappij; P.P. 782,194 (1935).
Condensation of $C_2H_2$ with toluenes to toluene.	$Cu_2Cl_2$ .	Koslow and Mogiljansky: <i>Zhur. Obshches Khim. (U.S.S.R.)</i> , 6 (68), 1897-1900 (1936).
Condensation of $C_2H_2$ with aromatic hydroxyl cpds.; phenol vapor: $C_2H_2=2:1$ to 20 g. vinyl phenyl ether per one l. of catalyst.	Zn or Cd salt of organic acids on active charcoal or pumice.	I. G. Farbenindustrie A.-G. (Reppe and Wolff); G.P. 643,220 (1937). U.S.P. 2,017,355 (1935). E.P. 430,590 (1935).

Table 14. Catalytic Condensation of Formaldehyde.

Reaction	Catalyst	Observer
Condensation of $CH_2O$ to a white crystalline polymer at room temp.	0.3% NaOH, CaO.	Mannish: <i>Ber.</i> , 52B, 160 (1919).
Condensation of $CH_2O$ (in sunlight) to sugars.	Mg, Zn.	Short, K. and Short, W. P.: <i>Biochem. J.</i> , 18, 1330 (1924).
Condensation of $CH_2O$ to reducing sugars.	Tropical sunshine.	Dhar, Rao and Ram: <i>Trans. Far. Soc.</i> , 27, 554-558 (1931).
Condensation of $CH_2O$ at room temp. and less than 200 mm.	Glass.	Spence: <i>J. Chem. Soc.</i> , 1933, 1193.
Condensation of $CH_2O$ .	Monose.	Kusin: <i>Ber.</i> , 68, 2169-73, (1935).
Condensation of $CH_2O$ plus urea.	Hexamethylenetetramine.	Pollak: B.P. 201,906, July 23, 1923.
Condensation of $CH_2O$ plus urea to an adhesive lacquer component.	$ZnCl_2$ .	Laucks, Inc.: B.P. 421,292, Jan. 2, 1935.
Condensation of $CH_2O$ plus urea.	Silica gel (oxides).	Wasum: U.S.P. 2,012,411, Aug. 27, 1935.
Condensation of 2 $CH_2O$ molecules followed by hydrogenation and dehydration processes to form straight-chain higher alcohols; the series of reactions is as follows:		Morgan: <i>Proc. Roy. Soc. London (A)</i> , 127, 246 (1930).



(most of the higher alcohols result from the condensation on a  $CH_2$  group; condensation on a  $CH_3$  group involves difficulties); condensation of 2 molecules of  $CH_2O$  with 1 molecule of acetaldehyde followed by dehydration and reduction to form branched chain alcohols follows the mechanism:



Condensation of HCHO with isobutyraldehyde to pentaglycol.

Alkaline substances retaining an amount of water between 20-60% (by weight).

Dupont (Walker and Turnbull): U.S.P. 2,135,063, Nov. 1. 1938.

Table 15. Catalytic Condensation of Aldehydes (Acetaldehyde, Propionaldehyde).

Reaction	Catalyst	Observer
Condensation of acetaldehyde.	HCl.	Fischer, E.: <i>Ber.</i> , 26, 2400 (1893); 27, 615 (1894).
Condensation of acetaldehyde to crotonic aldehyde.	H <sub>2</sub> SO <sub>4</sub> .	
Condensation of acetaldehyde; T. 100°.	Ethyl iodide.	Peachey: E.P. 4,263 (1914).
Condensation of acetaldehyde at 300° or below 300° to crotonic aldehyde.	Al <sub>2</sub> O <sub>3</sub> ; charcoal covered with TiO <sub>2</sub> (simultaneous dehydration and condensation).	Tschitschibabin: <i>J. Russ. Phys.-Chem. Soc.</i> , 47, 703 (1915); Konsortium für Elektrochemische Industrie: G.P. 349,915 (1922).
Condensation of acetaldehyde with aniline at 480-500°. $2\text{CH}_3\text{CHO} + \text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{CH}_2 \cdot \text{C}_6\text{H}_5\text{N} + 2\text{H}_2\text{O} + \text{H}_2$ .	Al <sub>2</sub> O <sub>3</sub> .	Tschitschibabin and Oparina: <i>Ber.</i> 60, 1873 (1927).
Condensation of acetaldehyde with H <sub>2</sub> S to thiophene and ethyl thiophene.	Al <sub>2</sub> O <sub>3</sub> .	
Condensation of acetaldehyde to aldol and crotonic aldehyde.	Base-exchanging cpds.	Selden Co. (Jaeger): E.P. 308,582, May 15, 1929; (Refer to C. 1929 II 4851). E.P. 304,640.
Condensation of acetaldehyde to aldol and crotonic aldehyde.		Selden Co. (Jaeger): E.P. 306,883, April 24, 1929; Can. P. 296,915, Jan. 21, 1930.
Condensation of propionaldehyde with NH <sub>3</sub> ; T. 250-260°, 97 g. tertiary bases, 40 g. nitroso-cpds. and 135 g. neutral salts; T. 310-320°, paravoline and 2-dimethyl pyridine.	Al <sub>2</sub> O <sub>3</sub> .	Oparina and Tschitschibabin: <i>J. Russ. Phys.-Chem. Soc.</i> , 54, 428,601 (1922). Oparina: <i>Ibid.</i> , 57, 319 (1925). Tschitschibabin and Oparina: <i>Ber.</i> , 60, 1877 (1927).
Condensation of aldehydes with NH <sub>3</sub> to pyridine bases; T. 200-350°.	Al <sub>2</sub> O <sub>3</sub> , Al(OH) <sub>3</sub> .	Tschitschibabin: <i>J. Russ. Phys.-Chem. Soc.</i> , 47, 703 (1915); 54, 411,413 (1922).
Condensation of crotonic aldehyde; 250 g. crotonic aldehyde converted into <i>o</i> -dihydrotoluyl aldehyde, octatrienal and small amount of dodecapentaenal; time, 30 hrs.; yield 25% of initial material; in isopropyl alcohol, isobutyl alcohol, isoamyl alcohol, and <i>n</i> -butyl alcohol, condensation starts considerably slower than in ethanol, methanol and propyl alcohol; solvents which do not contain special reactive groups, such as benzene, chloroform, dioxane, and acetic acid ester, slow down the condensation so much that after 24 hours only a weak yellow coloration appears, but no ppt.	2.5 cc. piperidine and glacial acetic acid (piperidine behaves essentially as the alcohols, while glacial acetic acid causes a very strong slowing down).	DuMont and Fleischhauer: <i>Ber.</i> , 71, 1958-1962 (1938).

Table 16. Catalytic Condensation of Aromatic Aldehydes (Benzaldehyde).

Reaction	Catalyst	Observer
Condensation of benzaldehyde with phthalic anhydride.	ZnCl <sub>2</sub> .	Fischer: <i>Ann.</i> , 206, 86 (1881).
Condensation of benzaldehyde with orthoethyl formate.	ZnCl <sub>2</sub> .	Fischer and Körner: <i>Ber.</i> , 17, 98 (1884).
Condensation of benzaldehyde with nitromethane.	ZnCl <sub>2</sub> .	Priebs: <i>Ann.</i> , 225, 321 (1884).
Condensation of benzaldehyde with chloral hydrate.	ZnCl <sub>2</sub> .	Boessneck: <i>Ber.</i> , 19, 367 (1886).
Claisen's condensation of aldehydes.	Alcohol-free aluminum alkoxides.	Tischtschenko: <i>J. Russ. Phys.-Chem. Soc.</i> , 38, 355-482 (1906).

Table 16 (Continued).

Reaction	Catalyst	Observer
Condensation of aromatic aldehydes to esters:	Alkali alkoxides.	Claisen: <i>Ber.</i> , <b>20</b> , 646 (1887).
$R \cdot CHO + R'CH_2ONa \rightarrow R \cdot CH(ONa)O \cdot CH_2R' \xrightarrow{+R \cdot CHO} R \cdot C \begin{array}{c} O \cdot CH_2R \\ \diagup \quad \diagdown \\ ONa \quad O \cdot CH_2R' \end{array} \xrightarrow{-R'CH_2ONa} R \cdot CO_2CH_2R$		
Condensation of cinnamic aldehyde and benzyl alcohol to cinnamic alcohol and benzaldehyde.	Al, benzyloxide (at the b.p.).	Poundorf: <i>Z. angew. Chem.</i> , <b>39</b> , 138 (1926). Verley: <i>Bull. soc. chim.</i> , <b>37</b> , 871 (1925).
Condensation of aldehydes.	Alkali benzylate.	Mastagli: <i>Compt. rend.</i> , <b>204</b> , 1656-1658 (1937).
Condensation of benzaldehyde with ethylisobutyrate and ethylacetate (condensation of $C_6H_5CHO$ with sodium malonic ester continues to the end, and gives off products only in the presence of basic catalysts or protons).	$(C_6H_5)_3CNa$ (basic catalyst).	Hauser and Breslow: <i>J. Am. Chem. Soc.</i> , <b>61</b> , 793-98 (1939).

Table 17. Catalytic Condensation of Ketones.

Reaction	Catalyst	Observer
Condensation of ketones (condensation of acetaldehyde to crotonic aldehyde).	HCl.	Fischer, E.: <i>Ber.</i> , <b>26</b> , 2400 (1893) <i>Ber.</i> <b>27</b> , 615 (1894).
Formation of diacetone alcohol from acetone or its decomposition to acetone.	$H_2SO_4$ .	
	Hydroxyl ions of bases.	Koelichen: <i>Z. physik. Chem.</i> , <b>33</b> , 129 (1900).
Condensation of ketones at 360° to 2 acetone molecules with simultaneous splitting off of 1 molecule $H_2O$ to mesityloxide; then condensation of 3 molecules of acetone and giving off of 2 molecules $H_2O$ to phoron.	$Al_2O_3$ (dehydration and condensation action).	Senderens: <i>Bull. soc. chim.</i> , <b>3</b> , 823 (1908). Maihle and de Godon: <i>Ibid.</i> , <b>21</b> , 61 (1917).
Condensation of acetone at high temp. and pressure to mesitylene, 1,3,5-xyleneol; T. 500-550°, only irreversible reaction; T. 350-400°, reversible and irreversible reactions.	Alumina.	Ipatieff and Petrow: <i>Ber.</i> , <b>60</b> , 753 (1927). Ipatieff and Petrow: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>59</b> , 429 (1927).
Condensation of acetone.	HCl.	Ipatieff, Dolgov and Wolnow: <i>Ber.</i> , <b>63</b> (1930). (refer to C1931 I 598 and C1931 II 1126.)
Condensation of fluorene with acetone to condensation product, a compound (I) of the formula $C_{19}H_{16}O$ formed by Michael's condensation of K fluorenyl with mesityl oxide; by heating with catalyst to fluorene, an isopropylidene fluorene is formed:	Solid KOH.	France, Maitland and Tucker: <i>J. Chem. Soc.</i> , <b>1937</b> , 1739-45.
	Na in xylene. K in benzene.	

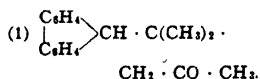


Table 18. Catalytic Condensation of Acids with Various Compounds.

Reaction	Catalyst	Observer
Condensation of phthalide with phthalic acid anhydride to dipthalide.	Na acetate.	Graebe and Guye: <i>Ann.</i> , <b>233</b> , 241 (1886).
Condensation of acetic acid with phthalic acid anhydride to phthalyl acetic acid.	K acetate.	Gabriel and Neumann: <i>Ber.</i> , <b>26</b> , 925 (1893).
Condensation of 2,000 kg. chlorbenzoic acid with aniline into phenylanthranilic acid.	1 kg. Cu.	Ulmann: <i>Ann.</i> , <b>355</b> , 316 (1907).

Table 18 (Continued).

Reaction	Catalyst	Observer
Knoevenagel's condensation of cinnamic aldehyde with maleic acid catalyzed by positive ions.	Amines and amino-acids; their action is stronger the higher the hydrogen conc.; the stronger basic secondary amines are more active than the primary amines; in water or alcohol solutions weak bases such as urea are inactive, but catalyze well in acid—acetic acid solution strongly dissociated.	Blanchard, Klein and McDonald: <i>J. Am. Chem. Soc.</i> , <b>53</b> , 2809-2810 (1931).
Condensation of oxy-stearic acid in $H_2$ atmosphere or in vacuum and equivalent amount of glycol to poly esters of a molecular weight, 1,000-40,000; T. 100-250°.	Mono-dichloroacetic acid, fumaric, phthalic, adipic acids.	Standard Oil Development Co.: F.P. 796,423, April 7, 1936.

Table 19. Catalytic Condensation of Alcohol with Hydrogen Sulfide.

Reaction	Catalyst	Observer
Condensation of alcohol vapors with $H_2S$ to mercaptans; T. 370-380°; 70% yield.	Oxides; $ThO_2$ has greater action than $Al_2O_3$ .	Sabatier and Mailhe: <i>Compt. rend.</i> , <b>150</b> , 1570 (1910).
Condensation of high molecular aliphatic or cycloaliphatic alcohols (at least 12 carbons) with $H_2S$ or S-containing gases; T. 300-340°.	Bauxite, $Al_2O_3$ , active charcoal, bleaching earth.	I. G. Farbenindustrie A.-G.: E.P. 454,668 (1937).

Table 20. Catalytic Condensation of Alcohol with Nitro Compounds.

Reaction	Catalyst	Observer
Condensation of alcohol with aniline vapors at 370-375° to form ethyl and diethyl aniline.	$ThO_2$ on asbestos.	Baukim, Chaudra and Roy: <i>J. Indian Chem. Soc.</i> , <b>5</b> , 383 (1928).
Condensation of alcohol with $NH_3$ to heterocyclic bases, such as pyridine.	Oxides on silica gel or containing $Al_2O_3$ ; $ZnO$ + silica gel or $Al_2O_3$ , silica gel, $ZnO$ and $Al_2O_3 = 72 : 20 : 10$ ; $CdO$ and silica gel and $Al_2O_3$ .	Deutsche Gold- und Silberscheideanstalt (Roessler): G.P. 565,798 (1932). G.P. 569,630 (1933).

Table 21. Catalytic Condensation of Alcohol with Olefins.

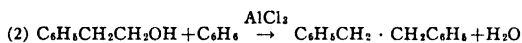
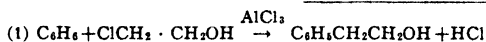
Reaction	Catalyst	Observer
Condensation of alcohol with olefins to form ethers; T. 250°; 20 atm. and more pressure.	$Al_2O_3$ , as well as phosphates or silicates with a heavy metal whose oxide is readily reduced, e.g., Cr or Ce metaphosphate, Ce salt of phosphorus tungstic acid with at least 10% free $H_3PO_4$ or phosphorus molybdic acid.	I. G. Farbenindustrie A.-G.: F.P. 710,846 (1931).
Condensation of alcohols with olefins, e.g., butyl alcohol plus ethylene = ethyl butyl ether.	Mixed catalyst consisting of kieselguhr or silicic acid and $H_3PO_4$ .	Universal Oil Products Co. (Ipatieff): U.S.P. 2,018,065 (1936).
Condensation of alkylene oxides and monovalent alcohols to glycol monoethylether.	Tertiary organic amines, for example, trimethyl- or amyl amine.	Distillers Co. Ltd. (Stanley and Jonell): E.P. 467,228, July 8, 1937.
Condensation of alkylene oxides or organic oxy-compounds with alcohol; T. 110-135°; 12-14 atm. pressure; to ethylene glycol monoethyl ether and diethyl glycol monoethyl ether.	$Al(OH)_3$ (partially dehydrated); also a catalyst in a partially hydrated form, such as yellow tungstic acid, should be present.	Distillers Co. Ltd. (Stanley, Jonell and Minkoff): F.P. 816,690, Aug. 13, 1937. E.P. 469,332, Aug. 19, 1937.

Table 22. Catalytic Condensation of Alcohol with Ketones.

Reaction	Catalyst	Observer
Condensation of alcohols with ketones: methyl alcohol and acetone to hexamethyl benzene; T. 400°.	$Al_2O_3$ .	Reckleben and Scheiber: <i>Ber.</i> , <b>46</b> , 2363 (1913).
High-pressure condensation at 400°; in addition to unsaturated and $O_2$ -containing substances a tarry-like mass is formed.	$Al_2O_3$ .	Ipatieff and Petrow: refer to Ipatieff on "Aluminum Oxide as a Catalyst in Organic Chemistry," p. 56, Leipzig, 1929.
Condensation of alcohol with acetone; T. 150-400°; treatment with air and $H_2O$ vapor; T. 450°.	$Al_2O_3$ impregnated with 15% Cu formate and 1.8% $MoO_3$ .	Deutsche Gold- und Silberscheideanstalt: G.P. 616,016 (1935).

Table 23. Catalytic Condensation of Alcohol with Benzene.

Reaction	Catalyst	Observer
Condensation of 2.2 parts cyclohexanol and 4 parts benzene; T. 200° for 6 hrs. to cyclohexylbenzene, or 3.2 parts benzyl alcohol and 4 parts benzene; T. 230° for 6 hrs. in autoclave to 40% diphenyl methane.	1 part chemically active bleaching earth.	Rheinische Kampfer Fabrik (Schöllkopf): G.P. 638,756 (1936). E.P. 319,205 (1929). F.P. 681,049 (1930).
Condensation of alcohols with benzene: 5 mols benzene with one mol $\beta$ -phenylethyl alcohol to dibenzyl; yield, 60.4%.	1 mol $\text{AlCl}_3$ .	Ishikawa and Maeda: <i>Science Reports Tokyo Bunrika Daigaku (A)</i> , 3, 157-64 (1937).



Besides, a resin originates from  $\beta$ -phenylethyl alcohol through splitting off of water; condensation of 1 mol 1-menthol and 5 mol benzene to *p*-menthene-3 and 3-phenylmethane.

Table 24. Catalytic Condensation of Benzene.

Reaction	Catalyst	Observer
Condensation of benzene and cyclohexene to cyclohexylcyclohexene ( $\text{C}_{12}\text{H}_{18}$ ) which may be hydrogenated to dicyclohexyl at room temp.; yield, 80-90%.	$\text{P}_2\text{O}_5$ (25 g.).	Truffault: <i>Compt. rend.</i> , 200, 406-408 (1935).
Condensation of benzene with propylene to propyl benzene.	Ni.	Wallach: <i>Ann.</i> , 381, 104 (1911).
Condensation of benzene with phthalic anhydride to <i>o</i> -benzoyl benzoic acid (of interest in the synthesis of anthraquinone).	Al powder (2 g. atoms) and $\text{HgCl}_2$ (2 g. molecules).	Gallay and Whitby: <i>Can. J. Research</i> , 2, 31 (1930).
Condensation of benzene vapors at 750° to diphenyl and 1,3-diphenyl benzene and 1,4-diphenyl benzene.	Al or Mg silicate (alkali free).	I. G. Farbenindustrie A.-G. (Tschunkur and Klein): U.S.P. 1,957,988 (1934).
Condensation of benzene and 20% diphenyl with 0.15-0.5% S; T. 650-950°; electrically heated tubes; 5-20% polyphenyl formed.	Tubes made of charcoal or graphite.	Dow Chemical Co. (Williams): U.S.P. 1,976,468 (1934).
Condensation of commercial benzene to diphenyl; T. 650-950°.	Heated carbon or graphite tube.	Dow Chemical Co. (Williams): U.S.P. 1,978,069 (1934).
Condensation of benzene with unsaturated hydrocarbons and their halide derivatives to alkyl derivatives.	$\text{P}_2\text{O}_5$ , $\text{H}_3\text{PO}_4$ (ethylene and propylene are adsorbed by benzene at 20°; faster at 80°).	Truffault: <i>Compt. rend.</i> , 202, 1286-1289 (1936).
Reaction between benzene and cyclohexene to form cyclohexylbenzene; yield, 65-68% (modified Claisen flask is used to prevent foaming).	Conc. $\text{H}_2\text{SO}_4$ .	Corson and Ipatieff: <i>Org. Syntheses</i> , 19, 36-37 (1939).

Table 25. Catalytic Condensation of Benzene.

Reaction	Catalyst	Observer
Condensation of hexene and benzene to hexylbenzene and dihexylbenzene.	Strong $\text{H}_2\text{SO}_4$ .	Spilker: <i>Ber.</i> , 23, 3169 (1890). Brochet: <i>Compt. rend.</i> , 117, 115 (1893).
Condensation of cracking benzene with olefinic cracking gases; T. 185°; 5 atm. pressure; the yield of cracking benzene increased by 55-60% (octane number increased from 70 to 75%).	$\text{H}_3\text{PO}_4$ on kieselguhr.	Universal Oil Products Co. (Ipatieff): U.S.P. 2,063,933 (1937).

Table 26. Catalytic Condensation of Phenols with Formaldehyde.

Reaction	Catalyst	Observer
Condensation of phenols with aliphatic aldehydes.	SnCl <sub>4</sub> .	Fabinyi: <i>Ber.</i> , 11, 283 (1878).
Condensation of phenols (Bakelite) with CH <sub>2</sub> O.	Substances of basic character, K <sub>2</sub> SO <sub>3</sub> .	Baekeland: G.P. 281,454 (1908).
Condensation of phenols with CH <sub>2</sub> O; T. less than 130°C.	N <sub>2</sub> bases; NH <sub>3</sub> .	Paqu��: Aust. P. 8,096, Oct. 28, 1909.
Condensation of phenols with CH <sub>2</sub> O=100 : 10-35 to syrupy condensation product.	N <sub>2</sub> bases; NH <sub>3</sub> .	Weichman: U.S.P. 1,218,146, March 6, 1917.
Condensation of phenols with CH <sub>2</sub> O; T. 350°; reaction time 24 hrs.; to 2,2- and 4,4-dihydroxydibenzyl amines.	29% NH <sub>3</sub> solution.	Shono: <i>Proc. World Eng. Congr. Tokyo</i> , 31, 533 (1929).
Condensation of phenols and cresol or mixtures of phenols and cresol with CH <sub>2</sub> O to resins (the dielectric constant of the product decreases when the content of phenol increases); a decrease in dielectric constant is obtained by heating the resins; condensation is effected to a higher degree by cresol than by phenol.		Stager: <i>Helv. Chim. Acta</i> , 14, 285 (1931).
Condensation of phenols with CH <sub>2</sub> O.	NH <sub>3</sub> ; mono-, di- and trimethylamine, ethylene diamine, hexamethylenetetramine, pyridine, NaOH, LiOH, KOH.	Holmes and Megson: <i>J. Soc. Chem. Ind.</i> , 52, 415-418 (1933).
Condensation of phenols with CH <sub>2</sub> O to a potentially reactive condensation product.	Alkali hydroxides; alkali carbonates.	Cherry: U.S.P. 1,994,753, March 19, 1935. Deutsch and Thom: U.S.P. 1,710,045, April 23, 1929.
Condensation of phenols with CH <sub>2</sub> O.	Alkalies.	Leysieffer: <i>Trans. Inst. Plastics Ind. (London)</i> (7), 4, 57 (1935).
Condensation of phenols with CH <sub>2</sub> O to crystal clear resin.	Alkalies.	Ostersetzer and Riesenfeld: G.P. 609,978, March 5, 1935.
Condensation of phenols with aldehydes.	Phosphoric acid.	Ipatieff and Komarewsky: Unpublished (U.O.P. Co)

Table 27. Catalytic Condensation of Phenols with Various Compounds.

Reaction	Catalyst	Observer
Condensation of phenols with phthalic anhydride.	SnCl <sub>4</sub> .	Baeyer: <i>Ann.</i> , 202, 154 (1880).
Condensation of phenols or polyphenols with aromatic amines.	SnCl <sub>4</sub> .	Calm: <i>Ber.</i> , 16, 2786 (1883).
Condensation of phenols with fatty acids.	ZnCl <sub>2</sub> .	Goldzweig and Kaiser: <i>J. prakt. Chem.</i> (2), 43, 91 (1891).
Condensation of phenols with H <sub>2</sub> S to thiophenol; yield only 3%.	Al <sub>2</sub> O <sub>3</sub> .	Sabatier and Maible: <i>Compt. rend.</i> , 150, 1570 (1910).
Condensation of unsaturated hydrocarbons with phenols, e.g., methyl alcohol; T. 200-300°; ordinary pressure; led through CaC <sub>2</sub> .	Charcoal or silicate.	Gesellschaft f��r Chemische Industrie (Basel): Swiss P. 131,812 (1927).
Condensation of phenols with alcohols to propylphenyl ether and o-propyl phenol by splitting off H <sub>2</sub> O; n-dipropyl ether and propylene is formed, the latter condensing to an unsaturated liquid hydrocarbon of polymethylene character under pressure.	Alumina.	Ipatieff, Orloff and Petroff: <i>Ber.</i> , 60, 1006 (1927).
Condensation of phenols with acetylene to synthetic resins.	H <sub>2</sub> SO <sub>4</sub> and Hg compounds.	Mathieson and Skirrow: <i>Plastics &amp; Molded Products</i> , 7, 231 (1931).

Table 27 (Continued).

Reaction	Catalyst	Observer
Condensation of phenols with ketones.	Phosphoric acid.	Ipatieff and Pines: Unpublished (U.O.P.)
Condensation of phenols: <i>m</i> -5-xyleneol, <i>m</i> -4-xyleneol, <i>o</i> -4-xyleneol, <i>o</i> -, <i>m</i> - and <i>p</i> -cresol, phenol, as well as brown-coal tar fractions; T. 170-230°; with CH <sub>2</sub> O.	Alkali catalysts; NH <sub>3</sub> , mono-, di- and tri-methylamine; mono-, di- and tri-ethylamine; <i>n</i> -, iso- and di- <i>n</i> -propylamine; mono- and di-benzylamine; ethylene diamine; hexamethylene; tetramine; pyridine; NaOH, LiOH, KOH.	Holmes and Megson: <i>J. Soc. Chem. Ind.</i> , <b>52</b> , 415-418 (1933).
Condensation of unsaturated hydrocarbons with phenols to phenol ether; T. 200°; pressure up to 25 atm.	Surface-active substances, such as silica gel, bleaching earth.	Shering-Kahlbaum A.-G. (Schoeller and Jordan): G.P. 598,298 (1934).
Condensation of phenols to resin (chlorine passed into the alkaline phenol solution).	NaOH, Ca(OH) <sub>2</sub> .	Chulkov: <i>Zhur. Khim. Prom.</i> (U.S.S.R.), <b>49</b> , (Nov. 1934).
Condensation of phenols or cyclic ketones with a carbonyl-containing substance to fusible oil-soluble resins.	Zn(OH) <sub>2</sub> , Ca(OH) <sub>2</sub> , Pb(OH) <sub>2</sub> , Co(OH) <sub>2</sub> , Mn(OH) <sub>2</sub> .	Rosenblum: B.P. 416,476, Sept. 10, 1934.
Condensation of phenols with cellulose, pentosans, pentoses and lignins to resins; T. 90-160°C.	NaOH.	Harris: <i>Iowa State Coll. J. Sci.</i> , <b>9</b> , 159 (1934).
Condensation of phenols with cellulose, pentosans, pentoses and lignins to resins.	ZnCl <sub>2</sub> .	Longwell and Maddocks: F.P. 774,998, Dec. 17, 1934

Table 28. Catalytic Condensation of Naphthalene.

Reaction	Catalyst	Observer
Condensation of $\alpha$ -benzyl naphthalene to benzanthrene; T. 650-800°; in the presence of water vapor; $\alpha$ -benzyl naphthalene : water vapor = 1 : 2.	Al <sub>2</sub> O <sub>3</sub> in mixture with other oxides or dehydrogenating catalysts; oxides of alkaline earths covered with anthracite.	I. G. Farbenindustrie A.-G. (Wulff, Koell and Krause): G.P. 594,564 (1925).
Condensation of naphthalene to dinaphthyl.	Silicic acid gel and aluminum gel with other substances forming mixed catalysts.	Rheinische Kampfer Fabrik: E.P. 319,205 (1929). F.P. 681,049 (1938).
Condensation of naphthalene.	Al <sub>2</sub> O <sub>3</sub> covered with anthracite.	I. G. Farbenindustrie A.-G.: G.P. 584,762 (1933). G.P. 586,878 (1933). F.P. 707,431 (1931).
Condensation of naphthalene.	25% Japanese acid earth.	Inoue and Ishimura: <i>Bull. Chem. Soc. Japan</i> , <b>9</b> , 431 (1934). Ishimura: <i>Bull. Chem. Soc. Japan</i> , <b>9</b> , 521 (1934).
Condensation of (1) naphthalene, anthracene, phenanthrene, etc.; (1) T. 100-130°.	Phosphoric acid anhydrides, oxyhalogenides, cpds. of BF <sub>3</sub> ; (1) a solution of Ag phosphate in H <sub>3</sub> PO <sub>4</sub> .	I. G. Farbenindustrie A.-G.: F.P. 793,250, Jan. 20, 1936. Meerwein and Pannwitz: <i>J. prakt. Chem.</i> , <b>141</b> , 123 (1934).
Condensation of diethylnaphthalene to monoethylnaphthalene.	Silicates treated with acids to obtain silicic acids or chemically activated bleaching earths.	Rheinische Kampfer Fabrik: G.P. 638,756 (1937). E.P. 319,205 (1929). F.P. 681,049 (1930).
Condensation of organic molecules; (Industrial process).	Chlorides of Al, Fe, Cr, Ti, Sn, Sb, Zn, Mg, Ca, as well as acetic acid anhydride, NH <sub>3</sub> , organic bases, Na, Na methylate, mineral acids, oxalic acid.	Cohn: "Laboratory Methods in Organic Chemistry," p. 629 4th Ed., Vol. II, Leipzig, 1907. Woker: "Katalyse" Vol. 1, p. 506. Sabatier: "Catalysis in Organic Chemistry," p. 284.

Table 29. Catalytic Condensation of Various Organic Compounds.

Reaction	Catalyst	Observer
Condensation of gases increased by surface extension.	Specific property of pure Pt.	Faraday.
Condensation of organic molecules; Friedel-Crafts reaction with removal of HCl or H <sub>2</sub> O also removal of hydrogen halide.	Cu and its cpds. are considered catalytic condensation agents for halogen-containing, especially aromatic organic cpds.	Agfa: G.P. 187,870; G.P. 202,170. Boehringer: G.P. 288,116. Ullmann: <i>Ann.</i> , <b>355</b> , 316 (1912); <b>350</b> , 83 (1907); <i>Ber.</i> , <b>38</b> , 2211 (1905). Bayer: G.P. 258,887 (1915); G.P. 162,824; G.P. 175,069.

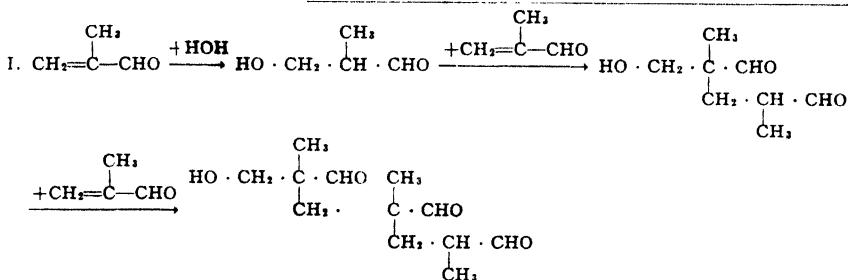


Table 29 (Continued).

Reaction	Catalyst	Observer
Condensation, polymerization and racemization, such as dinitrogenation, of nitrosotriacetoamine with phoron formation; (Industrial process).	Hydroxyl ions present in solutions of bases.	Francis and co-workers: <i>J. Chem. Soc.</i> , <b>101</b> , 2358 (1912); <b>103</b> , 1722 (1913); <b>107</b> , 1651 (1915).
Condensation of ethyl alcohol passed with air over heated Cu gauze and partially oxidized to aldehyde; when the mixture of alcohol and aldehyde is passed over Al at 360–460°, water and butadiene are formed.	Cu gauze.	Ostromyslenski: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>47</b> , 1494–1509 (1915); <b>35</b> , 70 (1916).
Condensation catalysis.	Al <sub>2</sub> O <sub>3</sub> (not glowed).	Rosenmund: <i>Fortschr. Chem., Physik, physik. Chem.</i> , <b>15</b> , 41–52, Oct. 1, 1919.
Condensation catalysis.	Al <sub>2</sub> O <sub>3</sub> (not glowed).	Adkins and Krause: <i>J. Am. Chem. Soc.</i> , <b>44</b> , 385–392 (1922).
Condensation catalysis.	Al <sub>2</sub> O <sub>3</sub> .	Rosenmund and Joithe: <i>Ber.</i> , <b>58</b> , 2054–2058 (1925).
Condensation of olefins.	BF <sub>3</sub> .	Hofmann and Otto: F.P. 632,768 (1927).
Condensation of cyclohexene with polynuclear aromatics.		Bodroux: <i>Ann. chim.</i> , <b>11</b> , 511 (1929).
Condensation of CO and NH <sub>3</sub> to HCN.	CeO <sub>2</sub> .	Bredig: <i>Z. Elektroch.</i> , <b>36</b> , 991, 1003, 1007 (1930).
Condensation of vinyl compounds: vinyl acetate, vinyl chloride with primary or secondary amines; 1 mol vinyl acetate : 2 mols methylamine; T. 300°.	Al <sub>2</sub> O <sub>3</sub> or bauxite.	I. G. Farbenindustrie A.-G. (Schmidt, Fries and Kollek): G.P. 528,466 (1931).
Condensation of methanol.	Alkali-containing catalyst.	Morgan, Hardy and Proeber: <i>J. Soc. Chem. Ind.</i> , <b>51</b> , 1–7 (1932).
Condensation of tar pretreated with CH <sub>2</sub> O; at ordinary temp., a plastic pitch for street paving is obtained.	Aqueous NH <sub>3</sub> led for 6 hrs. at 95°, FeSO <sub>4</sub> added, and air conducted at 100–200° for 25 hrs.	Broadhead and Andrews: U.S.P. 1,868,879, July 26, 1932.
Condensation of ethylene hydrocarbons at 350–700°F. under 40–100 atm. pressure; gaseous hydrocarbons condensed to liquid without cracking.	Pt and Pd black.	Pure Oil Co. (Wagner): U.S.P. 1,913,691, June 13, 1933.
Condensation of cyclohexane and acetyl chloride-containing cpd.	AlCl <sub>3</sub> .	Nenitzescu and Chicos: <i>Ber.</i> , <b>66</b> , 769–771 (1933).
Condensation of hydrocarbons.	Acid oxides not reducible to the metallic state under conditions of reaction and able to form many stages of valence, such as oxides of W, Mo, Mn, Cr, U, V; likewise together with other metal oxides, e.g., CeO <sub>2</sub> .	I. G. Farbenindustrie A.-G. (Kwell): G.P. 574,741, Kl 12o, April 20, 1933.
Condensation of polyhydric alcohols; T. 250–275°C.	Chlorides of Cu, Fe, Hg; ferric chloride.	Noak: B.P. 398,474, Sept. 6, 1933.
Condensation of aromatic hydrocarbons to diphenyl; T. greater than 700°.	Rare-earth metals or alkaline-earths covered with anthracite; Al <sub>2</sub> O <sub>3</sub> covered with anthracite.	I. G. Farbenindustrie A.-G. (Drossbach and Koell): G.P. 584,762 (1933). I. G. Farbenindustrie A.-G. (Roell): G.P. 586,878 (1933). F.P. 707,431 (1931).
Condensation of polymerisates obtained by polymerizing gaseous hydrocarbons, such as natural gas, pressure hydrogenation gas, or cracking gas with liquid hydrocarbons; T. 290 and 480° under ordinary and increased pressure.	Al <sub>2</sub> O <sub>3</sub> , fuller's earth; likewise a mixture with alkali oxides or alkaline-earth oxides.	Universal Oil Products Co. (Egloff): U.S.P. 1,988,112 (1935).

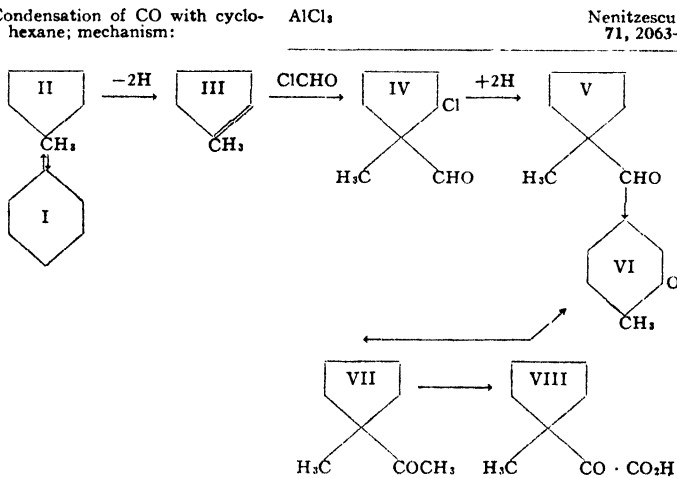
Table 29 (Continued).

Reaction	Catalyst	Observer
Poly-condensation of $\alpha$ -methyl acrolein to 2,4-dinitrophenylhydrazones (yellow oil); the mechanism proposed is as follows:	4% NaOH.  H <sub>2</sub> SO <sub>4</sub> .	Gilbert and Donleavy: <i>J. Am. Chem. Soc.</i> , <b>60</b> , 1737-1738 (1938). Gilbert and Donleavy: <i>Ibid.</i> , <b>60</b> , 1911-1914 (1938).



( $\alpha$ -methyl acrolein is distilled, water is brought into solution by adding alcohol and then the 4% NaOH is added); (much heat evolved cooling required); the reaction product is extracted with ether, dried with  $\text{Na}_2\text{SO}_4$  and after removing, the ether distilled under diminished pressure.

### Condensation of CO with cyclohexane: mechanism:



Aldehyde V was synthesized from VII over VIII and converted into VI with  $\text{AlCl}_3$ ; the formation of V from cyclohexanone with formyl chloride deviates in one point from that of higher acid chlorides, while otherwise the acid residue enters into 2-position to the  $\text{CH}_3$  group; in the case of formyl chloride, the addition follows in an opposite direction.

Condensation of cracking distillates from paraffin (the temp. is held uniform throughout the mass); for this purpose, to an already used condensation agt. by addition of fresh  $\text{AlCl}_3$  with steady and strong stirring the cracking product is allowed to flow gradually in; and condensation after addition of the total charge is continued until the iodine number of the reaction product is almost zero.

N. V. de Bataafsche Petroleum  
Mij:  
Dutch P. 44,472, Nov. 15, 1938.

Table 29 (Continued).

Reaction	Catalyst	Observer
Condensation of saturated carbonic acid ester with an organic carbonyl cpd. with a H atom at the carbonyl group or with ketones and aromatic aldehydes, e.g., to a suspension of 30.2 g. NaH in 460 cc. ethyl acetate is added 106 cc. benzaldehyde dropwise at 0°, acidified with CH <sub>3</sub> COOH; yield 149 g. ethyl cinnamate = 85% calculated with respect to benzaldehyde.	Alkali or alkaline-earth metal hydrides.	Dupont (Hausley): U.S.P. 2,158,071, May 16, 1939.

## PART XVII

## Catalytic Polymerization in Organic Chemistry

Table 1. Catalytic Polymerization of Ethylene.

Reaction	Catalyst	Observer
Polymerization of C <sub>2</sub> H <sub>4</sub> and other olefins to a viscous oil of empirical formula C <sub>8</sub> H <sub>12.5</sub> at ordinary temp. and under 70 atm. pressure; higher reaction temp. caused viscosity of crude hydrocarbon mixture to diminish.	BF <sub>3</sub> .	Butlerow and Gorianow: <i>Ann.</i> , 169, 147 (1873). Butlerow and Gorianow: <i>Ber.</i> , 6, 561 (1873).
Polymerization of commercial C <sub>2</sub> H <sub>4</sub> to lubricating oils; T. 150-300°C. (industrial process).	AlCl <sub>3</sub> (transformed into true organo-metallic cpds. resembling in some respects the Grignard cpds. of Mg. and showing marked activity toward O <sub>2</sub> and H <sub>2</sub> O).	Ipatieff: <i>Ber.</i> , 44, 2978 (1911). Ipatieff and Routala: <i>Ber.</i> , 46, 1748 (1913). Szayna: <i>Przemysl Chem.</i> , 12, 637 (1928). Stanley: <i>J. Soc. Chem. Ind.</i> , 49, 349T (1930). Petrov, Antzuz and Pozhiltzev: <i>Refiner Natural Gasoline Mfr.</i> , 12, 293 (1933).
Polymerization of C <sub>2</sub> H <sub>4</sub> to various hydrocarbons; T. 250-270°; 60-70 atm. H <sub>2</sub> pressure.	ZnCl <sub>2</sub> .	Ipatieff and Routala: <i>Ber.</i> , 46, 1748 (1913). Ipatieff and Routala: <i>J. Russ. Phys.-Chem. Soc.</i> , 45, 995 (1913).
Polymerization of C <sub>2</sub> H <sub>4</sub> .	H <sub>2</sub> SO <sub>4</sub> , KHSO <sub>4</sub> .	Klever and Fritz: <i>Mitt. chem.-tech. Inst. tech. Hochschule Karlsruhe</i> , 1, 1 (1923).
Polymerization of higher ethylene hydrocarbons.	Floridin.	Gurwitsch: <i>Kolloid-Z.</i> , 11, (1912). Gurwitsch: <i>Z. physik. Chem.</i> , 107, 235 (1923).
Polymerization of C <sub>2</sub> H <sub>4</sub> ; T. 400° C.; pressure, 40 atm.	Carbon (mild polymerization).	I. G. Farbenindustrie A.-G.: E.P. 261,393, Nov. 12, 1925.
Polymerization of C <sub>2</sub> H <sub>4</sub> to liquid products; T. 400-450°; high pressure; yield, 35-37%.	Al <sub>2</sub> O <sub>3</sub> .	Ipatieff: <i>J. Russ. Phys.-Chem. Soc.</i> , 63, 38 (1906). Ipatieff and Kljukwin: <i>Ber.</i> , 58, 4 (1925).
Polymerization of C <sub>2</sub> H <sub>4</sub> ; mostly C-formed; T. less than 650°C.	Borax.	Walker: <i>J. Phys. Chem.</i> , 31, 961 (1927).
Polymerization of C <sub>2</sub> H <sub>4</sub> .	Finely divided Ni.	Otto: <i>Brennstoff-Chem.</i> , 8, 321 (1927). Hoffmann: <i>Petroleum Times</i> , 23, 508 (1930).
Polymerization of gases containing 80% C <sub>2</sub> H <sub>4</sub> , 15% H <sub>2</sub> and 5% CO; T. 400-500°; pressure, 40 atm.; coke formation prevented by adding non-metal catalysts to silica gel (silica gel treated with boiling boron hydroxide solution and dried).	Silica gel covered with anthracite.	I. G. Farbenindustrie A.-G.: F.P. 630,344 (1927).
Polymerization of C <sub>2</sub> H <sub>4</sub> to butylene.	BF <sub>3</sub> ; BF <sub>3</sub> + Ni on a carrier.	Otto and Bub: G.P. 545,397, Oct. 12, 1928. U.S.P. 1,989,425, Jan. 29, 1935.

Table 1 (Continued).

Reaction	Catalyst	Observer
Polymerization of $C_2H_4$ and butylene to liquid hydrocarbons.	$AlCl_3$ (suspended in a petroleum solvent).	Ricard: U.S.P. 1,745,038, Jan. 28, 1928.
Polymerization of $C_2H_4$ to aliphatic and cyclic hydrocarbons.	$H_2SO_4 + 5\% H_2SO_4$ anhydride. $CuSO_4 + 2\% Hg_2SO_4$ .	Boeseken and Max: <i>Rec. trav. chim.</i> , <b>48</b> , 486 (1929).
Polymerization of $C_2H_4O$ to ether-like cpds. $(CH_2CH_2O)_n$ ; gaseous $C_2H_4O$ to solid polymeride and dioxane; polyethylene oxides more stable than polymethylenes (both well crystallized); ability to crystallize not confined to completely homogeneous substances, but is also possible with molecules of unequal length and similar structure.	Tertiary amines alkali metals, $SnCl_4$ (vapor).	Staudinger and Schweitzer: <i>Ber.</i> , <b>62B</b> , 2395 (1929).
Polymerization of $C_2H_4$ to liquids of composition $(CH_2)_n$ .	Atomic hydrogen.	Taylor and Hill: <i>Z. physik. Chem.</i> , <b>2B</b> , 449 (1929).
Polymerization of $C_2H_4$ .	$AlCl_3$ ; $BF_3$ .	Nash Stanley and Bowen: <i>Petroleum Times</i> , <b>24</b> , 799-802 (1930).
Polymerization of $C_2H_4$ .	$BF_3 + HI$ .	
Polymerization of $C_2H_4$ .	$BF_3 + HF$ (if $C_2H_4$ contains moisture). $BF_3$ (if $C_2H_4$ does not contain moisture).	Stanley: <i>J. Soc. Chem. Ind.</i> , <b>49</b> , 349T (1930). Storch: <i>J. Am. Chem. Soc.</i> , <b>54</b> , 4188 (1932); <b>56</b> , 374 (1934).
Polymerization of $C_2H_4$ .		Kassel: <i>Ibid.</i> , <b>54</b> , 3949 (1932).
Polymerization of $C_2H_4$ .		Lenher: <i>Ibid.</i> , <b>53</b> , 3752 (1931).
Polymerization of $C_2H_4$ .		Schneider and Frolich: <i>Ind. Eng. Chem.</i> , <b>23</b> , 1405 (1931).
Polymerization of $C_2H_4$ to rubber.	Hg (ultraviolet light).	Taylor: U.S.P. 1,746,168, Feb. 4, 1930. Bates and Taylor: <i>J. Am. Chem. Soc.</i> , <b>49</b> , 2438 (1927). Olsen and Meyers: <i>Ibid.</i> , <b>48</b> , 389 (1926).
Polymerization of $C_2H_4$ to lubricating oils with 10 to 45 C atoms; T. $180^\circ C$ . T. $230-275^\circ C$ .	$AlCl_3$ . $ZnCl_2$ .	Nash, Stanley and Bowen: <i>J. Inst. Petroleum Tech.</i> , <b>16</b> , 830 (1930).
Polymerization of $C_2H_4$ in the presence of petroleum ether.	$AlCl_3$ .	Stanley: <i>J. Soc. Chem. Ind.</i> , <b>34</b> , 349-354 (1930).
Polymerization of $C_2H_4$ to a mixture of paraffins, olefins and aromatic hydrocarbons; T. $700^\circ$ .	Silica gel.	Mailhe and Renaudie: <i>Compt. rend.</i> , <b>191</b> , 265 (1930).
Polymerization of $C_2H_4$ ; the degree of polymerization is roughly proportional to pressure.	Organo-metallic cpds.: Hg ethyl (metal alkyl decomposed).	Taylor and Jones: <i>J. Am. Chem. Soc.</i> , <b>52</b> , 1111 (1930).
Polymerization of $C_2H_4$ , as well as propylene and butylene.	$H_3PO_4$ or a phosphate on active charcoal or silica gel.	I. G. Farbenindustrie A.-G.: E.P. 340,515 (1930).
Polymerization of $C_2H_4$ to motor fuel.	$ZnCO_3$ .	Morgan, Ingleson and Taylor: <i>Petroleum Times</i> , <b>24</b> , 1024 (1931).
Polymerization of $C_2H_4$ .	$H_3PO_4$ , or a mixture of $H_2PO_4$ and $H_2SO_4$ .	Ipatieff and Komarewsky: (U.O.P. Co., 1933)
Polymerization of $C_2H_4$ to butylene; T. $200^\circ$ ; ordinary pressure; 19% ethylene converted into butylene.	1% Co on active charcoal prepared with $H_3PO_4$ calcined at $300^\circ$ .	I. G. Farbenindustrie A.-G. (Schuster): G.P. 559,736 (1933).
Polymerization of $C_2H_4$ ; T. $275^\circ$ ; pressure, 70 atm.	$ZnCl_2$ .	Ivanov: <i>Zhur. Priklad. Khim.</i> (U.S.S.R.), <b>6</b> , 103 (1933).

Table 1 (Continued).

Reaction	Catalyst	Observer
Polymerization of $C_2H_4$ thermally pretreated to highly unsaturated light oil; T. $370^\circ C$ .; pressure, 70 atm.; range of viscosity indices, from 50–100.	$AlCl_3$ .	Atkinson and Storch: <i>Ind. Eng. Chem.</i> , <b>26</b> , 1120 (1934).
Polymerization of $C_2H_4$ .	Organic alkali cpds.	I. G. Farbenindustrie A.-G.: G.P. 616,428, Kl 120, July 27, 1935; add to G.P. 597,496 (1934).
Polymerization of $C_2H_4O$ to dioxane; T. $120^\circ C$ .	Alkali hydroxides.	Webel: G.P. 597,496, May 25, 1934.
Polymerization of $C_2H_4O$ to earths.	Chemically-active bleaching earths.	I. G. Farbenindustrie A.-G.: G.P. 598,952 (1934).
Polymerization of $C_2H_4$ to light colored oils.	Tetraethyl lead (in benzene solution).	Cramer: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 1234 (1934).
Polymerization of $C_2H_4$ and propylene.	Alkali hydroxides (in inert solvents).	I. G. Farbenindustrie A.-G.: E.P. 406,443, March 1, 1934.
Polymerization of $C_2H_4$ under pressure.	$H_3PO_4$ .	Ipatieff and Pines: <i>Ind. Eng. Chem.</i> , <b>27</b> , 1364 (1935).
Polymerization of $C_2H_4$ ; T. $330^\circ$ .	$H_3PO_4$ .	Ipatieff and Pines: <i>Ind. Eng. Chem.</i> , <b>27</b> , 1364 (1935); refer also to Montmollin: <i>Bull. soc. chim.</i> , <b>19</b> , 242 (1916).
Polymerization of higher ethylene hydrocarbons.	Bleaching earth activated by heating at $150$ – $800^\circ$ ; moderately activated earths give high-polymer products at not too high temp.	Lebedew and Borgmann: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>5</b> , 67 (1935).
Polymerization of $C_2H_4O$ to dioxane; two ethylene oxide molecules unite to form dioxane at $180$ – $300^\circ$ .	$H_3PO_4$ on active kieselguhr or silica gel.	Universal Oil Products Company (Ipatieff): U.S.P. 2,018,065 (1935).
Polymerization of $C_2H_4$ ; purified by 4 methods: (1) over metal Na; (2) over $Ni+5\%$ $ThO_2$ at $25$ – $150^\circ$ and $Cu+ThO_2$ at $300$ – $350^\circ$ ; (3) prepared from $C_2H_5Br+Zn$ ; (4) prepared from alcohol by dehydration over $ThO_2$ at $350^\circ$ ; the fourth method shows the slowest polymerization; attributed to presence of small amounts of S cpds. originating from a catalyst; addition of about 0.1% $C_2H_5SH$ gave the same decrease in the reaction velocity.	Traces of oxygen.	Storch: <i>J. Am. Chem. Soc.</i> , <b>57</b> , 2598 (1935). Storch: (Refer to C. 1934 I 2875).
Polymerization of $C_2H_4$ over Co to light oil; *T. $150$ – $300^\circ$ ; above $300^\circ$ , $H_2$ , $CH_4$ and a large amount of C chiefly formed.	$Al_2O_3$ , silica gel+Cu, Co; Ni, most suitable; Fe and Fe—Cu, no marked catalytic action; *Co+kieselguhr, most suitable.	Konaka: <i>J. Soc. Chem. Ind. Japan</i> , <b>39</b> , 447B (1936).
Polymerization of $C_2H_4$ to liquid benzene of octane number 82 and containing paraffins, cycloparaffins, olefins and aromatics; T. $296^\circ$ and $324^\circ$ ; pressure, 35 atm.; contact time, 14,000 and 200 sec.; yield, 73.7% and 74.5%.	$H_3PO_4$ catalyst precipitated on active substances.	Ipatieff and Corson: <i>Ind. Eng. Chem.</i> , <b>28</b> , 860 (1936). Ipatieff and Corson: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>6</b> (68), 335–339 (1936).
Polymerization of $C_2H_4$ to a low-boiling liquid benzene with a high octane number.	$H_3PO_4$ on kieselguhr or silica gel; 2% $H_2TiO_3$ acts favorably.	Peters and Winzer: <i>Brennstoff-Chem.</i> , <b>17</b> , 366 (1936).
Polymerization of $C_2H_4$ ; T. $260^\circ$ ; yield, 40% (polymerization starts at $110^\circ$ ).	5 g. $P_2O_5$ +5 g. lamp soot; $P_2O_5$ more active than $H_3PO_4$ activity of the latter close to that of $AlCl_3$ .	Malischew: <i>Nefi</i> , <b>32</b> (19), 1–3 (1936).

Table 1 (Continued).

Reaction	Catalyst	Observer
Polymerization of $C_2H_4$ in two stages: at 350°C. at 60°C. oils having viscosity indices of 30-90 obtained.	Molybdc oxide. $AlCl_3$ .	Fuel Research Board, Report of 1936.
Polymerization of $C_2H_4$ .	(1) charcoal + 0.08% Fe. (2) charcoal + 0.36% Fe. (3) charcoal + 2.5 % Fe.	Klar: <i>Z. Elektroch.</i> , <b>43</b> , 379-389 (1937).
Polymerization of $C_2H_4$ under ordinary pressure: (1) marked formation of $CH_4$ , $H_2$ and C; T. 320°; (2) T. 290°; liquid polymers (moderate reduction, 60-65% favors formation of liquid polymers) ethylene content of gas mixture increases with a decrease in the activity of the catalyst; (3) T. 290°; yield, 235 cc./cm. liquid polymers; (4) T. 320°; yield, 290 cc./cm. liquid polymers; optimum gas velocity, 40 vol. $C_2H_4$ to 1 vol. catalyst; at higher velocity, a large part of $C_2H_4$ is converted into polymers.	(1) Co—Ag; low conc. and low temp. in the preparation favorable; prepared by ppt. from nitrates and washed with hot $H_2O$ ; reduction temp. at first 100°, then about 350°; catalyst masses precipitated with $K_2CO_3$ more readily reduced than when precipitated with other alkalis; Co—Ag gives larger amounts of liquid polymers than Co—Cu; (2) Co—Cu; 20% Cu or Ag content in Co most favorable; (3) Co + Ag + $U_3O_8$ + kieselguhr; ratio: 10 : 2 : 2 : 12; (4) Co + Ag + $U_3O_8$ + $ThO_2$ + kieselguhr; (5) Th—Zn.	Konaka: <i>J. Soc. Chem. Ind. Japan</i> , <b>40</b> , 236B-237B (1937).
Polymerization of $C_2H_4$ derivatives with $H_2SO_4$ in glacial acetic acid.	Acids; metals or metalloid halides; diarylethylene dimers depolymerize with $H_2SO_4$ and 4 mols $Br_2$ in $CHCl_3$ .	Schmitz-Dumont, Thömke and Diebold: <i>Ber.</i> , <b>70</b> , 175-182 (1937).
Polymerization of $C_2H_4$ ; T. 150-250°; pressure, 1200-1500 atm.; at 520 atm. pressure, polymers of molecular weight 2000 obtained; at 3000 atm. pressure, polymers of molecular weight 12,000 to 24,000 obtained.	0.1-5.0% $O_2$ .	Imperial Chemical Industries, Ltd.; Indian P. 23,709, July 3, 1937.
Polymerization of $C_2H_4$ to liquid olefins (in considerable amount) including butenes, hexenes and octenes which in turn polymerize to lubricating oil fractions; T. 250-300°C.	$AlCl_3$ (organo-metallic compounds); finely powdered Zn or Al increases the yield of free oil in $AlCl_3$ polymerizate.	Hall: Thesis, University of Birmingham (1937). Howes: E.P. 363,846 (1931).
Polymerization of $C_2H_4$ .	Ce metaphosphate.	
Polymerization of $C_2H_4$ ; T. 225°.	Ni.	
Polymerization of $C_2H_4$ .	Ultraviolet light.	
Polymerization of $C_2H_4$ .	Silent electrical discharge.	
Pressure polymerization of ethylene to gaseous product consisting of 39.5% hydrocarbons and 1.4% $H_2$ ; adsorption of ethylene at room temp. on the catalyst is very energetic, especially under pressure, and proceeds with such heat development that decomposition of $C_2H_4$ takes place, which may lead to a dangerous explosion; therefore work should be done on a small scale or in suitable solvent, for example, ethylated naphthalene.	$P_2O_5$ —lamp soot mass.	Malishev: <i>Oel Kohle Erdoel Teer</i> , 479-483 (1938).
Polymerization of ethylene; T. 300-400°.	Fe—Cu— $U_3O_8$ (the Fe catalyst prepared from the nitrate or the oxide); Ni catalysts prepared by reduction of $NiO$ in $H_2$ in the presence of other metals (polymerization activity of these catalysts depends on the reduction temp. and chiefly on the crystalline structure).	Konaka: <i>J. Soc. Chem. Ind. Japan (Suppl.)</i> , <b>41</b> , 22B-23B (1938).
Mixed polymers of ethylene with other polymerizable cpds., e.g., ethylene is heated with addition of $O_2$ , e.g., 0.2-0.4% $O_2$ or catalysts with isobutylene, styrene, stilbene, limonene, maleic acid diethyl ester, methyl methacrylate or other methacrylic acid esters, monomer vinyl cpds., butadiene, diethyl esters of fumaric, itaconic, or citraconic acid or their mixtures under high pressures, e.g., 500-2500 atm., T. 200-250°; depending upon the initial substances, elastic or soft masses suitable for artificial substances are obtained.	Benzoyl peroxide.	Imperial Chemical Industries, Ltd. (Perrin, Fawcett, Paton and Williams): E.P. 497,643, Jan. 19, 1939.

Table 1 (Continued).

Reaction	Catalyst	Observer
Polymerization of hydrocarbons (ethylene) (likewise for refining gasoline).	Phosphate containing minerals, phosphate slags mixed with adsorbents containing $\text{SiO}_2$ , e.g., diatomaceous earth; the mixture is moistened with fuming $\text{H}_2\text{SO}_4$ , molded and calcined until the acid vapors are removed.	Malishev: U.S.P. 2,148,634, Feb. 28, 1939 and U.S.P. 2,148,378, Feb. 21, 1939.
Polymerization of hydrocarbons of low molecular weight.	Heavy metal sulfides activated with sulfates (sulfides of Cu, Fe, Ni, Co, Tl, Bi, Pb, Mn, Hg, Mo, Cd, Zn, Sn, Ge, or Sb) oxidized partially to sulfates by air or mixed with metal sulfates.	Wassermann: E.P. 499,958, March 2, 1939.
Polymerization of gaseous or liquid hydrocarbons to fuels; trimethylethylene polymerized to diamylene; likewise, cracking of dicyclopentadiene to cyclopentadiene; the same catalysts may be used in the diene syntheses (Diels-Alder), for example, in the preparation of dicyclopentadiene from cyclopentadiene.	Sulfides of various metals are treated with $\text{O}_2$ or air for 2 months or a mechanical mixing together of sulfides and sulfates, wet or dry; in addition, the mixtures may be treated afterward with S or liquid organic or inorganic S cpds.	Wassermann: F.P. 838,379, March 3, 1939.
Polymerization of gaseous olefins, e.g., ethylene is led at 90–260° through a tower filled with filling bodies and a polymerization catalyst dissolved or suspended in a liquid solvent is permitted to flow in a counter-current; polyvalent alcohols, such as propylene glycol, high-boiling monovalent alcohols, nitroparaffins, or halogen hydrocarbons as liquid media; to the catalyst suspension a volatile oil is added to take up the reaction heat, e.g., a heavy fraction obtained by polymerization or an illuminating oil.	$\text{AlCl}_3$ (in ethylene chloride). $\text{NaAlCl}_4$ (in halogenated octane or nonane). $\text{Al}_2\text{O}_3$ or $\text{SiO}_2$ .	Process Management Co., Inc. (Atwell): U.S.P. 2,146,667, Feb. 7, 1939
Polymerization of $\text{C}_2\text{H}_4$ ; T. 80–100°.	Pt.	Farkas: <i>Trans. Faraday Soc.</i> , <b>35</b> , 906–17 (1939).
Polymerization of $\text{C}_2\text{H}_4$ .	$\text{AlCl}_3$ powder (prepared from Al and dry HCl gas).	
Polymerization of $\text{C}_2\text{H}_4$ .	$\text{BF}_3$ and $\text{H}_2$ halides, except HF, or alkyl or aryl halides.	

Table 2. Catalytic Polymerization of Propylene.

Reaction	Catalyst	Observer
Polymerization of $\text{C}_3\text{H}_6$ ; T. 25°C.	97% $\text{H}_2\text{SO}_4$ .	Preston: <i>J. Soc. Chem. Ind.</i> , <b>40</b> , 145 (1921).
Polymerization of $\text{C}_3\text{H}_6$ and isobutylene at room temp. under pressure.	Clays, floridin.	van Winkle: <i>J. Am. Pharm. Assoc.</i> , <b>17</b> , 544 (1928).
Polymerization of $\text{C}_3\text{H}_6$ to liquids; T. 650°C. to solids; T. 700–720°C.	Oxides, silica gel.	Maihle and Renaudie: <i>Compt. rend.</i> , <b>191</b> , 851 (1930).
Polymerization of $\text{C}_3\text{H}_6$ ; propylene is passed at 350° under atmospheric pressure over dehydrated florida earth; activity of catalysts increased and maintained for a long time, when propylene is led with traces of HCl, e.g., in the form of an alkylchloride; polymerized product, a liquid, $d=0.7$ , which, when distilled with water vapor, gives 90% of a colorless, readily volatile motor fuel, practically free from resin-	Florida earth treated with HCl; synthetic Al silicate acts similarly; silicates of Fe and Mg and precipitated $\text{SiO}_2$ , inactive precipitated porous $\text{SiO}_2$ on the surface of which $\text{Al}_2\text{O}_3$ is adsorbed, about 20 times more active than the best florida earth; activity of catalyst $\text{Al}_2\text{O}_3$ on $\text{SiO}_2$ decreases 50% after 7 days; polymerization reactions poisoned by alkalis and oxygen (short time), also by water vapor.	Gayer: <i>Ind. Eng. Chem.</i> , <b>25</b> , 1122–1127 (1933).

Table 2 (Continued).

Reaction	Catalyst	Observer
forming substances, of octane number 87; in this distillation product a series of homologs, such as olefins ( $C_3$ to $C_9$ ) (b.p. up to $150^\circ$ ) are present, also small amounts of paraffinic hydrocarbons.		
Polymerization of $C_3H_6$ .	$H_3PO_4$ ; solid $H_3PO_4$ .	Ipatieff: <i>Ind. Eng. Chem.</i> , <b>27</b> , 1067 (1935). Ipatieff, Schaad and Corson (U.O.P.): Unpublished.
Polymerization of $C_2H_4$ under 10 kg./cm. <sup>2</sup> pressure.	Solid catalysts prepared from mixtures of $H_3PO_4$ and $P_2O_5$ (1:1); carriers: diatomaceous earth, florida earth, silica gel, activated charcoal, petroleum coke, cerium metaphosphate (tested on ethylene only).	Ipatieff and Schaad (U.O.P. Co.).
Polymerization of $C_3H_6$ under 10 kg./cm. <sup>2</sup> pressure.	Solid $H_3PO_4$ ; catalysts prepared from 75%, 89% and 100% $H_3PO_4$ with one or more substances: alumina, $ZnO$ , $ZnCl_2$ , $Na_2Al_2O_4$ , $MgO$ , $MgCl_2$ , $NiCl_2$ , $CuCl_2$ , diatomaceous earth, florida earth, silica gel, activated charcoal, petroleum coke, sawdust.	Ipatieff and Schaad (U.O.P. Co.).
Polymerization of $C_3H_6$ under pressure.	Liquid catalysts prepared from: (1) 89% and 100% $H_3PO_4$ ; (2) 100% $H_3PO_4$ with 1% $H_2SO_4$ . (3) 89% and 100% $H_3PO_4$ with promoters such as Cd phosphate, Cd acetate, Cu sulfate, $CuCl$ , K boron fluoride, cyclohexane and a fraction from a straight-run naphtha (b.p. $140-170^\circ C.$ ).	Ipatieff and Schaad (U.O.P. Co.).
Polymerization of a mixture of $C_3H_6$ and butenes; T. $150^\circ$ (lower temp. required than for polymerization of propylene alone); pressure, 10 atms.	Solid $H_3PO_4$ .	Ipatieff: <i>Ind. Eng. Chem.</i> , <b>27</b> , 1067 (1935). Ipatieff: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>6</b> , (68), 327-334 (1936).
Polymerization of $C_3H_6O$ to wax-like high polymer products; as solvents are used those which do not react with the oxide i.e., aliphatic or hydroaromatic, hydrocarbons.	Alkali-acting catalysts.	I. G. Farbenindustrie A.-G.: G.P. 616,428, Kl 12o, July 27, 1935; add to G.P. 597,496.
Polymerization of $C_2H_4$ ; T. $290-310^\circ$ ; yield, 64.4% liquid products (b.p. in the interval of ordinary motor benzene).	$ZnCl_2$ on pumice.	Brandes, Gruse and Lowy: <i>Ind. Eng. Chem.</i> , <b>28</b> , 554-559 (1936).
Polymerization of $C_3H_6$ .	Double salts of $AlCl_3$ with halides of Li, Be, Ts, V, Cr, Mn, Ti, Co, Ni, Mg on carriers.	Standard Oil Co. (Kuentzel): U.S.P. 2,082,500 (1937).
Polymerization of $C_3H_6$ and butylene; T. $150-400^\circ F.$ ; pressure 14-210 atm.	$HgAl_2Br_3$ , $SbAlBr_3$ or $BiAlBr_3$ .	Standard Oil Co. (Ruthruff): U.S.P. 2,082,518, June 1, 1937.
Polymerization of $C_3H_6$ and butylene-containing gases; T. $450-550^\circ$ pressure 14-70 atm.	Double salts obtained by melting together metal halides, such as: Na, Li, Ca, Ba and Cu chloraluminate; Na, Hg, Sb and Ti bromaluminate.	Standard Oil Co. (Ruthruff and Kuentzel): U.S.P. 2,082,520, June 1, 1937.
Polymerization of $C_3H_6$ , isobutylene and butylene cracking gases in the presence of alkapolylene in which one or more $H_2$ atoms are replaced by polar groups, such as $NH_2$ , Cl, Br, S, $COOH$ , $NO_2$ , $OH$ , e.g., chloroprene, geraniol, acids from Chinese charcoal, to viscous masses which serve to	Florida earth, $BF_3$ , $BF_3 \cdot HF$ , $AlCl_3$ , $AlCl_3 \cdot CH_3NO_2$ , benzoyl peroxide.	N. V. de Bataafsche Petroleum Mij: F.P. 819,619, Oct. 22, 1937.



Table 2 (Continued).

Reaction	Catalyst	Observer
improve the viscosity of lubricating oils: 22.5 g. isobutylene + 2.5 g. chloroprene; T. $-80^{\circ}$ ; the product, in amount 4.4%, when added to a lubricating oil, increases its viscosity index from 26 to 111.	$\text{BF}_3$ .	
Polymerization of $\text{C}_3\text{H}_6$ at $350^{\circ}$ C. under pressure.	Floridin, $\text{Al}_2\text{O}_3$ on porous silica.	
Polymerization of propylene; T. $480-600^{\circ}$ ; pressure, 1-50 atms.; impossible to obtain good yield of liquid propylene polymers; optimum temp., $520^{\circ}$ ; at pressures above 40 atms., 87-90% of the converted propylene obtained as a liquid product, 70-80% of which boils below $150^{\circ}$ .	Iron walls of the vessel; precipitated coke and high molecular weight reaction products strongly catalyze the reaction; iron walls are strongly catalytic at $480^{\circ}$ , but at $600^{\circ}$ the action is almost insignificant.	Mützenhändler: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , 7 (69), 1848-1857 (1937).
Polymerization of $\text{C}_3\text{H}_6$ (obtained by dehydrating a constant boiling commercial isopropyl alcohol over $\text{Al}_2\text{O}_3$ at $450^{\circ}$ ); T. $260-350^{\circ}$ ; pressure, 170-410 atms. three-stage polymerization: (1) the formation of a dimer; (2) the dimer reacts with a further amount of $\text{C}_3\text{H}_6$ , forming trimers; (3) the trimers combine with $\text{C}_3\text{H}_6$ to form tetramers; the products obtained change from dimers to heavy polymers above $300^{\circ}$ ; below this limit the composition of the products depends only on the extent of polymerization of the initial product (from pure dimers to 35% dimers on completion of the reaction).	Dilute $\text{H}_3\text{PO}_4$ (conc. 10-50%).  $\text{H}_3\text{PO}_4$ (above 30%).	Monroe and Gilliland: <i>Ind. Eng. Chem.</i> , 30, 58-63 (1938).
Polymerization of $\text{C}_3\text{H}_6$ .	Silicic acid gel prepared by precipitation of a silicate solution with an acid and dehydrated to a 45-55% water content at a temp. below $100^{\circ}$ (3-4 mol $\text{H}_2\text{O}$ per mol $\text{SiO}_2$ ); this partially dehydrated gel is washed with water and then treated with a 0.1-1 mol Al salt solution ( $\text{AlCl}_3$ ) at $100^{\circ}$ for 1 hour, whereby formation of Al silicate takes place; the gel so activated is washed with $\text{H}_2\text{O}$ , dried and used for polymerization of gaseous olefins.	Phillips Petroleum Co. (McKinney): U.S.P. 2,142,324, Jan. 3, 1939; refer also to U.S.P. 2,147,985, Feb. 21, 1939.

Table 3. Catalytic Polymerization of Butylenes.

Reaction	Catalyst	Observer
Polymerization and dehydrogenation of butylene to rubber.	Cu followed by Na.	Perkin and Weizmann: E.P. 9,722, April 21, 1911.
Polymerization of butylene to naphthenic liquids; T. $-10^{\circ}\text{C}$ .	$\text{AlCl}_3$ .	Weizmann and Legg: U.S.P. 1,395,620, Nov. 1, 1922.
Polymerization of butylene and trimethyl ethylene to 80% dimers and 20% higher polymers.	$\text{H}_2\text{SO}_4$ .	I. G. Farbenindustrie A.-G.: E.P. 322,102, Dec. 1, 1928.
Polymerization of butylene to 33% liquid products containing unsaturated hydrocarbons and aromatic hydrocarbons; T. $650-700^{\circ}$ .	Silica gel.	Mailhe and Renaudie: <i>Compt. rend.</i> , 192, 429 (1931). Mailhe and Renaudie: <i>J. usines gas.</i> , 54, 569 (1930).
Polymerization of butylene.	$\text{H}_3\text{PO}_4$ .	Ipatieff and Corson: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , 6 (68), 335-339 (1936).
Polymerization of butylenes: 1-butene and isobutene, both with 30% $\text{H}_3\text{PO}_4$ .	Solid $\text{H}_3\text{PO}_4$ on diatomaceous earth.	Ipatieff and Schaad (U.O.P. Co.).

Table 3 (Continued).

Reaction	Catalyst	Observer
Polymerization of a refining waste gas to liquid polymers of butylene; T. less than 66°; polymerize hydrogenated over Ni to substances which, when added to benzene, increase the octane number.	60-75% H <sub>2</sub> SO <sub>4</sub> .	Standard Oil Development Co.: P.P. 814,360, June 21, 1937.
Polymerization of butylene in the cold; T. 20-35°; isobutylene is adsorbed as a reactionable olefin, the amount of which depends:	60-70% H <sub>2</sub> SO <sub>4</sub> .	McAllister: <i>Oil and Gas J.</i> , 36 (26), 139-142 (1937). McAllister: <i>Refiner Natural Gasoline Mfr.</i> , 16, 493-496 (1937).
(a) on the strength of the acid (not higher than 70% H <sub>2</sub> SO <sub>4</sub> should be used, otherwise <i>n</i> -butylene is adsorbed also);		
(b) on the ratio of acid to alcohol;		
(c) on the temp. which should be maintained between 20 and 40° to prevent preliminary polymerization; about 90% isobutylene is adsorbed, and the acid phase which it saturates is separated from the hydrocarbon phase and polymerized by passing through heated spiral tubes at 100°; reaction completed in about 1 minute; with 65% H <sub>2</sub> SO <sub>4</sub> , 75% diisobutylene and 25% trimers obtained; mild hydrogenation of diisobutylene results in the formation of isooctane.		
Polymerization of a mixture of butenes; the octane number is higher by about 3.5 units than that of pure <i>n</i> -butene or pure isobutene; the octanes from <i>n</i> -butene consist of 2,4- and 2,5-dimethylhexane, 2-methylheptane and 3,4-dimethylhexane, while those from isobutene consist essentially of 2,2,4-trimethylpentane, and those of <i>n</i> -butene-isobutene mixtures consist essentially of 2,2-dimethylhexane and 2,2,3-trimethylpentane: T. 95-120; T. 120°-177°, 7.8 atm. pressure; T. 147°, pressure 42 atm., yield, 70.55%, 74-80% and 88%; hydrogenation of octene gave octane mixtures with octane numbers: 98-100; 83-85, 95-97 and 95.	H <sub>3</sub> PO <sub>4</sub> .	Ipatieff and Schaad: <i>Ind. Eng. Chem.</i> , 30, 596-599 (1938).

Table 4. Catalytic Polymerization of Isobutylene.

Reaction	Catalyst	Observer
Polymerization of isobutylene.	H <sub>2</sub> SO <sub>4</sub> .	Butlerow and Gorianov: <i>Ann.</i> 169, 143 (1873).
Polymerization of isobutylene to olefin-rich paraffins and naphthenes; T. 325-400°C.	Al.	Ipatieff and Dovgolevich: <i>J. Russ. Phys.-Chem. Soc.</i> , 43, 1431 (1911).
Polymerization of isobutylene.	H <sub>2</sub> SO <sub>4</sub> .	Lebedev and Koblyanski: <i>Ber.</i> , 63, 103 (1930).
Polymerization of isobutylene.	H <sub>2</sub> SO <sub>4</sub> , 60-70%.	N. V. de Bataafsche Petroleum Mij: P.P. 737,743 (1931).
Polymerization of isobutylene to high molecular weight products; T. -80°C.	BF <sub>3</sub> .	Zelinsky, Denisenki, Evontova and Khromov: <i>Sintet. Kauchuk (U.S.S.R.)</i> , 4, 11 (1933).
Polymerization of isobutylene to oils.	AlCl <sub>3</sub> .	Waterman, Over and Tulleners: <i>Rec. trav. chim.</i> , 53, 69° (1934).
Polymerization of isobutylene to polymers containing cyclic cpds.	Al <sub>2</sub> O <sub>3</sub> on silica gel. AlCl <sub>3</sub> .	Waterman, Leendertse and de Kok: <i>Ibid.</i> , 53 (4), 115 (1934); 53 (4), 151-158 (1934).
Polymerization of isobutylene.	Cu or glass tube filled with activated alumina.	Ipatieff and Corson: <i>Ind. Eng. Chem.</i> , 27, 1069 (1935). Corson: <i>Ind. Eng. Chem.</i> , (B) 6, 297 (1934).
Polymerization of isobutylene.	Silica gel greater than kaolin greater than floridin; sequence of activity.	Slobodin: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , 8, 35 (1935).
Polymerization of isobutylene and simultaneous conversion of <i>n</i> -butylene to isobutylene; T. 300°.	Ton, Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , silicate-H <sub>3</sub> PO <sub>4</sub> . H <sub>3</sub> PO <sub>4</sub> -charcoal (most active).	Frost, Kudkovsky and Serebrjakova: <i>Doklady Akad. Nauk S.S.S.R.</i> , 4, 373-375 (1936).
Polymerization of isobutylene with aqueous mineral acid to 83% diisobutylene and 17% triisobutylene; T. 150-250°.	H <sub>2</sub> SO <sub>4</sub> , 3-10%.	N. V. de Bataafsche Petroleum Mij: P.P. 815,379, July 10, 1937.
Polymerization of: (1) <i>tert.</i> butyl phenol with polyisobutylene to <i>tert.</i> octyl phenol then decomposition to butyl phenol and isobutylene; T. 120°;	AlCl <sub>3</sub> , tonsil.	Dow Chemical Co. (Perkins and Nutting): U.S.P. 2,091,565, Aug. 31, 1937.

Table 4 (Continued).

Reaction	Catalyst	Observer
(2) 1410 g. phenol and 560 g. diisobutylene to butyl phenol; T. 120°; time, 2 hrs.; yield, 64.5%.	AlCl <sub>3</sub> (45 g.).	
Polymerization of mixtures of isoolefins, such as isobutylene and isopropyl ethylene with other olefins; a very low temp. used so that only isoolefins polymerize before an increase in temp. so that polymerization of other olefins may begin; then the catalyst is decomposed by adding 95% alcohol, glycol, glycerol, ethyl or methyl ether, methanol, isopropyl alcohol acetone, methylethyl ketone or furfural.	BF <sub>3</sub> , BCl <sub>3</sub> , AlCl <sub>3</sub> (a metal halide hydrolyzed by water).	Standard Oil Co. (Webb): U.S.P. 2,099,090, Nov. 16, 1937.
Continuous polymerization of isobutylene, isoprene, styrene, indene at -10°, -40° and up to -150°:	BF <sub>3</sub> , AlCl <sub>3</sub> , ZnCl <sub>2</sub> , TiCl <sub>4</sub> , the organic complex compounds or double compounds of halides.	Standard Oil Development Co.: F.P. 826,993, April 13, 1938.
(1) monomer is introduced into a mixture of diluents (ethane, propane, butane, their mixtures, ethylene) with the catalyst;		
(2) then the 3 components are continuously led into the reaction vessel and the mixture of the polymerizate and diluting agent is withdrawn to an equal extent.		
Polymerization of isobutylene at room temp. after hydrogenation; the paraffin hydrocarbon mixture obtained is very unstable at 435° and under action of 1 min.; likewise the ring cpds. which originated by polymerization; the number of rings of the reaction product is smaller than that of the initial material; Penn. mineral oil subjected to the same conditions showed no decrease in the number of rings after treatment; polymerization products obtained from cyclohexene after heating to 435° appeared more stable than those obtained from isobutylene, especially no destruction of rings followed; natural cyclic oils of approximately the same molecular weight were found only slightly more stable with respect to polymerization products obtained from cyclohexene.	AlCl <sub>3</sub> .	Waterman and Leendertse: <i>J. Inst. Petroleum Tech.</i> , 25, 32-40 (1939).
Polymerization and alkylation of isobutylene for the preparation of motor fuels with a high octane number; selective polymerization of isobutylene is effected within a temp. interval 100-220° and at ordinary pressure (to avoid corrosion of the apparatus), also in the presence of olefins; contact time a few seconds; polymerization leads to the formation of 2,4,4- $\alpha$ -trimethylpentane and 2,4,4- $\beta$ -trimethylpentane; the amount of olefins converted in one passage is 20-56%, while the polymerization product contains 50-86% diisobutylene in addition to triisobutylene; the triisobutylene may be split readily into diisobutylene over bentonite at a suitable temp.	Simultaneous application of a gaseous (HCl), as well as a solid catalyst (Al <sub>2</sub> O <sub>3</sub> ); HCl as a catalyst is used in small amounts (below 1% by volume with respect to isobutylene) and may be easily regained; the solid Al <sub>2</sub> O <sub>3</sub> catalyst may be regenerated optionally.	Natta and Baccaredda: <i>Chimica e l'industria (Italy)</i> , 21, 393-418 (1939).

Table 5. Catalytic Polymerization of Amylenes.

Reaction	Catalyst	Observer
Polymerization of amylene to di-amylene.	Clays, floridin.	Gurwitsch: <i>J. Russ. Phys.-Chem. Soc.</i> , 47, 827 (1915).
Polymerization of amylene.	H <sub>2</sub> SO <sub>4</sub> .	Norris and Joubert: <i>J. Am. Chem. Soc.</i> , 49, 873 (1927).
Polymerization of amylene.	H <sub>2</sub> SO <sub>4</sub> (1.86).	Ormandy and Craven: <i>J. Inst. Petroleum Tech.</i> , 13, 317 (1927).
Polymerization of amylenes obtained from the fermentation of alcohol.	Floridin.	Lebedev, Windogradow and Wolshinski: <i>J. Russ. Phys.-Chem. Soc.</i> , 60, 441 (1928).

Table 5 (Continued).

Reaction	Catalyst	Observer
Polymerization of amylene.	H <sub>3</sub> PO <sub>4</sub> .	Ipatieff and Pines (U.O.P. Co.).
Polymerization of amylene.	Clays, floridin.	Gayer: <i>Ind. Eng. Chem.</i> , <b>25</b> , 1122 (1933).
Polymerization of amylenes (rapid); T. —80°C.	AlCl <sub>3</sub> .	Leendertse, Tulleners and Waterman: <i>Rec. trav. chim.</i> , <b>53</b> , 715 (1934).
Polymerization of amylenes to polymers of partly cyclic structure; T. —80°C.	AlCl <sub>3</sub> .	Waterman, Leendertse and Klazinga: <i>Ibid.</i> , <b>54</b> , 1679-1684 (1935).

Table 6. Catalytic Polymerization of Olefins (Industrial Process).

Reaction	Catalyst	Observer
Polymerization of olefins at room temp. under atmospheric or higher pressure.	BF <sub>3</sub> (in glass vessels).	Butlerow: <i>Ber.</i> , <b>9</b> , 1605 (1876). Butlerow: <i>Ann.</i> , <b>189</b> , 44 (1877).
Polymerization of liquid olefins from cracked crudes to synthetic lubricating oils; use of a preliminary, light refining treatment prior to polymerization has been suggested.	AlCl <sub>3</sub> .	Brownlee: E.P. 141,753 (1919). E.P. 414,237 (1934). E.P. 399,646 (1932). U.S.P. 1,309,432, July 8, 1919. U.S.P. 1,374,277 (1918).
Polymerization of olefins.	BF <sub>3</sub> + finely powdered metals, especially Ni; BF <sub>3</sub> may be completely regenerated from reaction products by the action of heat.	Hoffman and Otto: E.P. 293,487 (1927). U.S.P. 1,811,130 (1931).
Polymerization of olefins under pressure.	BF <sub>3</sub> in the presence of water, halogen acids or halogenated hydrocarbons capable of reacting with benzene in Friedel-Crafts synthesis.	Hoffman, Otto and Stegemann: E.P. 313,067 (1928). E.P. 307,802, March 12, 1929. U.S.P. 1,885,060, Oct. 25, 1932. U.S.P. 1,933,434 (1929).
Polymerization of gaseous hydrocarbons, such as ethylene and propylene, into liquid hydrocarbons heated under pressure of 40 to 120 atm. at 260-540°.	AlCl <sub>3</sub> , AlBr <sub>3</sub> or other metal halides; Pd-Pt sponge; finely divided alloys or metals of the 8th group; silica gel, active charcoal, fuller's earth.	Pure Oil Co.: F.P. 680,038, April 24, 1930.
Polymerization of olefins.	Metal halides of the 3rd group.	N. V. de Bataafsche Petroleum Mij: F.P. 716,159, April 27, 1931.
Polymerization of olefinic hydrocarbons by organic acids.	Amylene + CCl <sub>4</sub> · COOH Amylene + (COOH) <sub>2</sub> .	Ipatieff and Pines (U.O.P. Co.).
Polymerization of gaseous olefins.	H <sub>3</sub> PO <sub>4</sub> ; promoters: AlCl <sub>3</sub> , PCl <sub>3</sub> , PCl <sub>5</sub> , NiO, NiCl <sub>2</sub> .	Ipatieff and Komarewsky (U.O.P. Co.).
Polymerization of olefinic hydrocarbons.		Egloff, Schaad and Lowry: <i>J. Phys. Chem.</i> , <b>35</b> , 1825-1903 (1931).
Polymerization of olefins to lubricating oils.	AlCl <sub>3</sub> .	Sullivan, Jr., Vorhees, Oak and Barnard: <i>J. Soc. Automotive Engrs.</i> , <b>29</b> , 40 (1931).
Polymerization of gaseous olefins.	AlCl <sub>3</sub> and other inorganic halides in combination with organic polar compounds (nitrobenzene) and with inactive metal halides (NaCl).	N. V. de Bataafsche Petroleum Mij (Elkington): E.P. 358,068 (1931).
Polymerization of gaseous olefins.	Florida earth impregnated with AlCl <sub>3</sub> .	Howes: E.P. 372,763 (1932).
Polymerization of olefins.	Halides, Al.	Barnard: <i>Natl. Petroleum News</i> , <b>24</b> , 62 (1932).
Polymerization of olefins to lubricating oils; also cracking of heavy oils to motor fuels.	AlCl <sub>3</sub> (McAfee method for preparing AlCl <sub>3</sub> involves chlorination of a mixture of coke and bauxite at 850°).	Kränzlein: "Aluminium Chlorid in der organischen Chemie," 1932. refer also to Calloway: <i>Chem. Rev.</i> , <b>17</b> , 327 (1935).

Table 6 (Continued).

Reaction	Catalyst	Observer
Polymerization of unsaturated cpds. contained in petroleum refinery outlet gases, such as styrene, indene, cyclopentadiene, butadiene, etc.	Al <sub>2</sub> O <sub>3</sub> .	Odell: U.S.P. 1,925,151 (1933)
Polymerization of unsaturated hydrocarbons; at room temp. very little reaction between CH : CN; at 100° adsorption and reaction very rapid—no liquids obtained; in the presence of Et <sub>2</sub> O vapor a liquid product results; C <sub>2</sub> H <sub>2</sub> bubbled through Et <sub>2</sub> O and then passed over; an extremely exothermic reaction results in the formation of liquid products which decompose violently with H <sub>2</sub> O to give HCl and a dark brown cuprene-like material; C <sub>2</sub> H <sub>4</sub> adsorbed slowly by AlCl <sub>3</sub> (red oil); Et <sub>2</sub> O or PhNMe <sub>2</sub> · AlCl <sub>3</sub> complex causes no reaction between C <sub>2</sub> H <sub>2</sub> and AlCl <sub>3</sub> ; a darkening of the catalyst occurs indicating AlCl <sub>3</sub> · C <sub>2</sub> H <sub>2</sub> ; Al <sub>2</sub> Cl <sub>6</sub> Et <sub>2</sub> OC <sub>2</sub> H <sub>2</sub> and Al <sub>2</sub> Cl <sub>6</sub> · 2PhNMe <sub>2</sub> fail to catalyze the polymerization of C <sub>2</sub> H <sub>2</sub> at room temp. or at 100°; Me <sub>3</sub> N completely stops adsorption of C <sub>2</sub> H <sub>2</sub> by AlCl <sub>3</sub> ; at 100° darkening ceases; isobutylene very reactive toward AlCl <sub>3</sub> ; liquid products formed immediately; theory of polymerization based on the electronic structure of AlCl <sub>3</sub> and olefins postulated.	AlCl <sub>3</sub> .	Hunter and Johe: <i>J. Am. Chem. Soc.</i> , <b>55</b> , 1248-1252 (1933).
Polymerization of olefins; C <sub>2</sub> H <sub>4</sub> is subjected to 130 atm. pressure for 10 hrs. in the presence of catalysts; if the olefins contain moisture, the polymerization may be carried out, using BF <sub>3</sub> and HF, or BF <sub>3</sub> alone.	BF <sub>3</sub> and hydrogen halides except HF or alkyl or aryl halides; BF <sub>3</sub> and EtCl or BF <sub>3</sub> and HI (an oily product results).	Hoffman, Otto and Stegemann: G.P. 504,730, March 24, 1933. G.P. 507,919, April 28, 1933.
Polymerization of unsaturated hydrocarbons.	Organic alkali compounds.	Ziegler and Jakob: <i>Ann.</i> , <b>511</b> , 45-63, 64-88, 89-100, 101-109 (1934).
Mechanism of polymerization and depolymerization of olefins; an optional sequence following additions on the olefin molecules of positive hydrogen ions and positive organic groups corresponding to the hydrogen ions; polymerization of isobutylene to diisobutylene and triisobutylene mixtures; the state existing in each step of polymerization is given by the following equation: $\text{H} \\ \text{:C:C:} + \text{H}^+ \rightleftharpoons \text{:C:C:}^+$		Whitmore: <i>Science</i> , <b>79</b> , 45-47 (1934).
Polymerization of gaseous olefins, generator gas, water gas, etc.; T. 600-1200°; T. 700-800° especially favorable.	Al <sub>2</sub> O <sub>3</sub> .	Greenstreet: F.P. 762,184 (1934). E.P. 412,933 (1934).
Polymerization of gaseous olefins to aromatic hydrocarbons (polymerized over dehydrogenation catalysts at 600°; T. 300-500°; pressure, 40 atm.	Active charcoal or silicate gel.	I. G. Farbenindustrie A.-G. (Wietzel and Pfandler): U.S.P. 1,910,910 (1934).
Polymerization of olefins to high molecular weight olefins; T. 20-25°C.	BF <sub>3</sub> (with Ni); ZrCl <sub>4</sub> , TaCl <sub>5</sub> .	Ipatieff and Grosse: <i>J. Am. Chem. Soc.</i> , <b>57</b> , 1616 (1935).
Polymerization of gaseous olefins at 200° under pressure (with ethylene, the reaction starts at 120°); intermediate product, monopropyl ester $2\text{CH}(\text{CH}_3)_2 \cdot \text{PO}(\text{OH})_2 \rightarrow \text{CH}_3\text{CH}_2\text{C} \cdot \text{CH}(\text{CH}_3)_2 + 2\text{PO}(\text{OH})_2$	Liquid H <sub>3</sub> PO <sub>4</sub> .	Ipatieff: <i>Ind. Eng. Chem.</i> , <b>27</b> , 1067-1069 (1935).
Polymerization of gaseous olefins (butylene) at 130°; for mixed olefins, lower temp. and acid conc.; polymerization velocity increases in the series: propylene, α-butylene, β-butylene, isobutylene.	Liquid H <sub>3</sub> PO <sub>4</sub> (100%).	Ipatieff and Corson: <i>Ind. Eng. Chem.</i> , <b>27</b> , 1069-1071 (1935).
Polymerization of gaseous olefins.	Aqueous neutral or acidified solutions of metal chlorides, ZnCl <sub>2</sub> , FeCl <sub>3</sub> , etc., on fuller's earth.	Universal Oil Products Company (Morrell): U.S.P. 2,039,440 (1935). U.S.P. 2,030,070 (1936).

Table 6 (Continued).

Reaction	Catalyst	Observer
Polymerization of gaseous olefins with more than two C atoms to liquid hydrocarbons, separated from the unchanged ethylene by selective polymerization or alkylation and converted into acetylene at a temp. greater than 1100°, under pressure, in less than 0.1 sec.		Universal Oil Products Company (Morrell): U.S.P. 2,030,070 (1936).
Polymerization of gaseous olefins.	Highly active clay, such as the montmorillonite type, treated with acid; 50-100% must pass through 200-mesh sieve.	Texaco Development Corp. (Halpern, Logan, Manley and Ullrich): Can. P. 342,155 (1935).
Polymerization of gaseous hydrocarbons to higher liquid hydrocarbons.	Hg or Cd vapors led over highly heated graphite or coke catalyst.	I. G. Farbenindustrie A.-G. (Winkler and Häusler): G.P. 626,338 (1935).
Polymerization of gaseous olefins from the cracking process to liquid benzene hydrocarbons; T. 50-350°; pressure, 1.75-70 atm.	H <sub>3</sub> PO <sub>4</sub> on kieselguhr, silica gel, activated bleaching earths containing active charcoal.	Universal Oil Products Company (Ipatieff): U.S.P. 2,057,433 (1936).
Polymerization of olefins to liquid hydrocarbons.	H <sub>3</sub> PO <sub>4</sub> + kieselguhr calcined by heating between 180-400°.	Universal Oil Products Company (Ipatieff): Can. P. 360,570, Sept. 15, 1936.
Polymerization of olefins; T. 150-250°; by hydrogenation of the polymerization products of isobutylene, isooctane and isododecane are obtained.	H <sub>2</sub> SO <sub>4</sub> , HCl, H <sub>3</sub> PO <sub>4</sub> , H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> , H <sub>2</sub> AsO <sub>4</sub> , benzene sulfonic acids, acid-reacting salts, such as Ag <sub>2</sub> SO <sub>4</sub> , PbSO <sub>4</sub> , Cu <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> , or AlCl <sub>3</sub> , ZnCl <sub>2</sub> , MgCl <sub>2</sub> .	International Hydrogenation Patents Co., Ltd.: F.P. 794,397 (1936).
Polymerization of olefins.	NaAlCl <sub>4</sub> , LiAlCl <sub>4</sub> .	Standard Oil Co. (Kuentzel): U.S.P. 2,082,454, June 1, 1937.
Polymerization of unsymmetrical gaseous olefins with 4 to 8 C atoms such as isobutylene, trimethyl ethylene or methyl-ethyl ethylene at 70° under pressure.	Solutions of FeCl <sub>3</sub> , ZnCl <sub>2</sub> or AlCl <sub>3</sub> in methyl, ethyl, or isopropyl alcohol.	Phillips Petroleum Co.
Polymerization of gaseous olefins such as propylene or isobutylene to liquid hydrocarbons boiling below 170° at 25° under ordinary pressure.	A mass consisting of silica gel and AlCl <sub>3</sub> placed on a wire cylinder rotated rapidly; the gases are led from the inside of the cylinder and passed through the catalyst mass from which they are thrown as liquid polymers.	Phillips Petroleum Co. (Frey): U.S.P. 2,079,935, May 11, 1937.
Polymerization of olefins to liquid polymers; T. 800-900°F.; pressure, greater than 35 atm.		Phillips Petroleum Co. (Guyer): U.S.P. 2,087,540, July 20, 1937.
Polymerization of olefin-containing gases; T. 650-950°.	Active charcoal, silica gel or fuller's earth; air conducted vapors of Se are led into the contact space for a short time (5-30 min.).	Texas Co. (Towne): U.S.P. 2,011,385 (1937).
Polymerization of olefins; T. 200-800°F.; pressure, 3.5-140 atm.	NaAlCl <sub>4</sub> on carriers: pumice, coke (regenerated by spraying with a solution of NaAlCl <sub>4</sub> , drying and treating with Cl <sub>2</sub> ).	Standard Oil Co. (Ruthruff): U.S.P. 2,082,519, June 1, 1937.
Polymerization of unsaturated gaseous hydrocarbons; T. 350°; pressure, 25 atm.	H <sub>3</sub> PO <sub>4</sub> on chamotte (best catalyst) (the catalyst prepared by heating to 250° consists chiefly of pyrophosphoric acid which shows better catalytic properties than H <sub>2</sub> PO <sub>4</sub> ; by heating to a higher temp. (600°) the activity decreases).	Rudkowski, Schewzowa and Poemeller: <i>Prom. Org. Khim.</i> (U.S.S.R.), 3, 332-335 (1937).
Polymerization of olefins with less than 9 C atoms, such as propylene and $\beta$ -isobutylene; as solvents are used inert liquid agents (acetone), cooling agents (liquid CO <sub>2</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub> , CH <sub>2</sub> Cl <sub>2</sub> ).	BF <sub>3</sub> or HF.	Shell Development Co. (McSimo and Hilmer): U.S.P. 2,085,524, June 29, 1937.

Table 6 (Continued).

Reaction	Catalyst	Observer
Polymerization of olefins ( $C_7-C_{12}$ ); indicates a strong branched structure of the dimers and trimers and does not deal with intermediate compounds of polymerization in the actual sense of the word, but rather with substances which may be considered for structural reasons as those that do not permit further polymerization; with higher olefins ( $C_7-C_{12}$ ), the polymerization stopped with products of a gas oil character and formed essentially the dimers in the experiments with propene besides benzene and gas oil fractions, lubricating oil fractions (up to 15%) were obtained; polymerization of propene over $P_2O_5$ also gives unsaturated compounds with a branched chain; an increase in temp. and time over $AlCl_3$ permits further polymerization of the gas oil fraction, resulting in the formation of a lubricating oil of viscosity 3.0 only.	$P_2O_5$ .	Yostes and Bartels: <i>Oil Kohle Erdöl Teer</i> , 13, 1166-1172 (1937).
Polymerization of cracked gases; T. 225-325°; atm. pressure, time, 19 cc./min.; yield, 46%; by diluting with $H_2$ the yield of liquid products decreases; cracked gas obtained by vapor-phase cracking of gas oil at 650° to olefins: 1% $C_2H_4$ , 69.6% $C_3H_6$ , 19% $C_4H_8$ and 10.4% higher olefins; time, 33 cc./min.; yield, 53.5%.	50 g. $H_3PO_4$ precipitated on pumice.	Otsuka: <i>J. Soc. Chem. Ind. Japan</i> 40, 21B-22B (1937).
Polymerization of gaseous olefins, e.g., mixtures of propylene, isobutylene and <i>n</i> -butylene are stepwise and selectively polymerized over the catalyst (1); isobutylene is polymerized to isooctenes at 20-66°, then the <i>n</i> -butylenes to octene mixtures at 66-121°, finally propylene above 121°, especially 205-260°, under 6.5-20 atm. pressure; also in the first stages it is worked under such a pressure (3-24 atm.) that butylenes are in liquid phase; the unsaturated polymers are hydrogenated to the saturated hydrocarbons, especially 2,2,4- and 2,2,3-trimethylpentane.	Solid calcined $H_3PO_4$ .	Universal Oil Products Co.: F.P. 830,036, Nov. 26, 1937.
Polymerization of 80% gaseous olefins: 45% $C_2H_4$ and 35% $C_3H_6$ to gasoline of density 0.77 at 60°F. and octane number, 80-81; T. 230°.	Cd phosphate: Cu orthophosphate: $H_3PO_4$ (1 : 1 : 4) or Cd phosphate: $H_3PO_4$ (1 : 3).	Anglo-Iranian Oil Co., Ltd. (Dunstan): E.P. 460,659, March 4, 1937. F.P. 810,846, March 31, 1937.
Polymerization of a mixture of olefins: 30.4 g. <i>tert</i> .-butanol + 10.2 g. <i>sec</i> .-butanol followed by hydrogenation; T. 99°; time 20 min.; yield, 86.5% (81% dimers); if started from <i>sec</i> .-butanol only, no polymers are formed.	44.3% $H_2SO_4$ .	N. V. de Bataafsche Petroleum Mij: F.P. 810,155, March 17, 1937.
Polymerization of a mixture of olefins: 74.1 g. <i>tert</i> .-butanol + 117.2 g. <i>tert</i> .-amyl alcohol to nonylenes, chiefly 3,5,5-trimethylhexene-2; also 2,4,4-trimethylhexene-2, and 2,3,4,4-tetramethylpentene-1; T. 80-100°; pressure, 7-11 atm.; hydrogenated to an anti-knock substance; T. 280-300°; pressure, 14-18 atm. and 150 atm.	13.46% $H_2SO_4$ (95%).	
	Ni formate in mineral oil.	
Polymerization of gaseous olefins.	Calcined mixture of kieselguhr, adsorbing earth and $H_3PO_4$ ; the latter is the chief part of the mixture.	Universal Oil Products Company (Ipatieff): Can. P. 371,511, Jan. 25, 1938.
Polymerization of olefins from products of a low polymerization degree; T. 180-300°; 99% propylene is led over the catalyst at a rate of 20 cc./hr./cm <sup>3</sup> catalyst space; yield 96% by volume (b.p. up to 200°).	$AlF_3$ prepared from 100 cc. water-containing $AlF_3$ hydrate corresponding to 50 g. anhydrous $AlF_3$ ; grains, 2-5 mm.; dried in an electric oven at 220°.	I. G. Farbenindustrie A.-G.: E.P. 478,601, Feb. 17, 1938. F.P. 823,373, Jan. 19, 1938.
Polymerization of olefins to considerably more viscous oils with lower Br number than in the absence of water.	$AlCl_3$ or other Friedel-Crafts catalysts in the presence of water.	Shell Development Co. (Perquin): U.S.P. 2,117,498, May 17, 1938.
Polymerization of olefins in liquid phase (in benzene); from light hydrocarbons such as ethylene; light oils obtained from heavy olefins such as heptylene; viscous lubricating oils formed under pressure; T. 180-275°.	Alkyl compounds of Pb or Hg especially Pb tetraalkyl.	General Motors Corporation (Cramer): U.S.P. 2,117,022, May 10, 1938.

Table 6 (Continued).

Reaction	Catalyst	Observer
Polymerization of gaseous olefins; the butane-butylene mixture is cracked and the gaseous mixture, consisting principally of butylene and $H_2$ , is separated by condensation of butylene, the latter being catalytically polymerized to di- and trimeric butylene; the dimer polymerizate is hydrogenated to saturated hydrocarbons representing anti-knock substances; the trimer products are depolymerized catalytically and then added to the polymerized product or converted into high molecular weight products (m. w. above 1000) by a special polymerization process.	$H_2SO_4$ .	Standard Oil Development Co. (I. G. Farbenindustrie A.-G.): F.P. 822,790, Jan. 7, 1938.
Polymerization of olefins with 4 or 5 C atoms, whereby tertiary olefins are chiefly polymerized; two stages: (1) T. 149–218° (2) T. greater than 593°; tertiary olefins, inclined more to the formation of high polymers and asphalt-containing substances at high temp., are separated in the first stage.	$H_3PO_4$ .	N. V. de Bataafsche Petroleum Mij: F.P. 823,242, Jan. 17, 1938. E.P. 479,657, March 10, 1938.
Polymerization of gaseous olefins to benzines: (1) T. 149° and 371°; the reaction mixture is cooled to a (2) T. 32–92° (3) T. 149° polymerization carried out with very small amounts of condensation agents because the polymerizate precipitated out in a pure state may be recirculated.	$BF_3$ (complex compounds formed between $BF_3$ and the polymerizate).	Standard Oil Co.: F.P. 823,270, Jan. 18, 1938.
Polymerization of unsaturated aliphatic hydrocarbons to high molecular weight alcohols, ethers, esters and salts; these compounds are esterified and the esters formed converted into alcohols, ethers, and salts of alkyl sulfuric acid.	Polymerization catalysts; $H_2SO_4$ , alkalies, water.	N. V. de Bataafsche Petroleum Mij: E.P. 479,137, March 3, 1938.
Polymerization of olefins, also alkylation of cyclic cpds. with olefins; the same catalyst may be used in the condensation of ethers or alcohols with aromatics, phenols and aldehydes; the catalyst is also suitable for halogenation of unsaturated cpds. and isomerization reactions; catalyst serves for the formation of esters or the conversion of carboxylic acids with olefins.	A mixture of 80% $H_3PO_4$ (90%) and 20% kieselguhr is heated to about 450–510° (a 10% loss in wt.) treated with vapor at 225–250° and the $H_4P_2O_7$ formed is converted into $H_3PO_4$ (the pyrophosphoric acid is converted into the orthophosphoric acid).	Universal Oil Products Co. (Ipatieff and Schaad): U.S.P. 2,120,702, June 14, 1938.
Polymerization of hydrocarbons.	$H_3PO_4$ ; catalyst regenerated by treating with air at 450–510° whereby combustible precipitates are oxidized; at 200–275° the catalyst is treated with vapor to effect partial hydration of $P_2O_5$ and to induce the necessary activity to the catalyst.	Universal Oil Products Co. (Ipatieff and Corson): U.S.P. 2,113,654, April 12, 1938.
Polymerization of gaseous olefins; during polymerization the gas stream is made smaller or the temperature is increased, whereby the yield in benzine is raised; likewise the gas mixture may be led first through wide and then through narrow tubes filled with the catalyst, whereby the narrower tubes are heated to a higher temp. than the wide ones.	Usual catalysts.	Ruhrchemie A.-G. (Velde): Austrian P. 104,101, June 23 1938.
Polymerization of olefins, e.g., ethylene, propylene, butylenes, amylene, nonylene, dodecylene,	A mixture of ortho- (1) and pyrophosphoric (2) acid whose $D^{18}$ lies between 1.90 and 1.99, e.g.,	I. G. Farbenindustrie A.-G.: F.P. 829,916, July 11, 1938. E.P. 491,932, Oct. 6, 1938.



Table 6 (Continued).

Reaction	Catalyst	Observer
pentadecylene, also cyclohexene, diolefins, and vinyl acetylene; for example, propylene T. 170-200°; pressure, 25-30 atm.	composition between 68 (1) + 32 (2) and 24 (1) + 72 (2); the mixture may be placed also on carriers, such as bone charcoal or silica gel and may be applied in mixture with heavy metal salts (Cu, Ni, Ag); the mixture, by heating in vacuum of 85% orthophosphoric acid (com.), may be brought to the desired density.	
Polymerization of gaseous olefins; mixtures of gaseous hydrocarbons, such as cracking gases or products obtained by dehydrogenation of unsaturated hydrocarbons, especially propane-butane fraction, are led over the catalyst in liquid phase under pressure up to 50 atm. at 10-160°; polymerization occurs in one step and the polymerizate is separated in intermediate columns; the gases dehydrogenated are added to the fresh gas in ratio 1 : 1 to 5 : 1; benzine with octane number 80, heavy benzine, and lubricating oil are obtained.	Al silicate.	Soc. An. Française pour la Fabrication des Essences et Pétroles (Houdry and Lassiat); F.P. 828,714, May 27, 1938.
Polymerization of gaseous hydrocarbons; from the initial cracking gases the propane-butane fraction is separated under pressure in a condensation zone, together with gaseous hydrocarbons separated from the polymerization products; it is then polymerized at high temp. and pressure to benzine; from the total remaining gaseous residue ( $H_2$ , $CH_4$ , $C_2H_6$ ) the polymerizable $C_3$ - $C_4$ parts are washed out by means of gas oil.		Polymerization Process Corp. (Robinson and Roberts, G., Jr.); U.S.P. 2,118,822, May 31, 1938.
Polymerization of olefins to isobutylene, (I) and <i>n</i> -butylene to isooctylene; T. 65-150°; pressure (14-42 atm.) under which isobutylene remains liquid; 1-10% by volume of triisobutylene (II) is added; the products are fractionated, part of the II is returned, the remainder splitting chiefly to I at 205-235° over a catalyst (or at 230-260° without a catalyst); I is likewise returned to the polymerization zone.	60-75% $H_2SO_4$ .	Standard Oil Development Co.; F.P. 49,047, Oct. 14, 1938; add to F.P. 814,360; (Refer to C. 1937 II 3996).
Polymerization and condensation of olefins; T. 100-200°; also under high pressure; olefins, or mixtures containing such, may be polymerized or condensed with an aromatic or partially hydrogenated aromatic cpd. as naphthalene or phenols; isobutylene gives at 175° di- and tri-isobutylene; with phenol, it gives isobutylphenol (F. 99°); from isododecylene and phenol, dodecylphenol (b.p. 195-200°) is obtained; from isononylene and cresol, crude isononyl cresol is obtained.	Florida earth.	I. G. Farbenindustrie A.-G.; E.P. 480,756, March 24, 1938.
Polymerization of gaseous hydrocarbons; gases containing olefins are heated (425-590°); this temp. is not sufficient to produce essential polymerization when mixed with an $O_2$ -containing gas; however, it is sufficient to effect oxidation; on the addition of $O_2$ -containing gas, the temp. of the hydrocarbon gas is so far raised that polymerization takes place (620-730°); thereby water or water vapor is added and the reaction gases are held for 5-50 seconds under 0.7-7 atm. at the polymerization temp.; thereafter the reaction products (heavy hydrocarbons) are separated on cooling; the gases may be preheated to 480-650° and then heated through $O_2$ to the cracking temp. (705-815°), followed by cooling by the addition of water at the polymerization temp.	Heteropoly- acid or its acid salts, e.g., phosphor tungstic acid or phosphor molybdic acid; likewise with addition of a heavy metal salt (Cu, Ag, Ni).	Pure Oil Co. (Maschwitz); Can. P. 374,890, July 5, 1938.
Polymerization of unsaturated hydrocarbons; a mixture of gaseous hydrocarbons rich in ethylene is converted into higher gaseous olefins in the presence of $O_2$ , halogens, S, $SO_2$ , or $SiCl_4$ at 395-650° under 1-7 atm. during 10 sec.; the mixture obtained is converted into liquid hydrocarbons, especially benzine, under a high pressure (28-200 atm.) at about the same temp.; if 0.5-3% $O_2$ is added in the first stage, then olefin oxides, e.g., ethylene oxide, are formed which act as polymerization catalysts in the second stage; olefin oxides may be added especially for the polymerization, as well as for the polymerization of resin-formers in cracked benzine, for the second stage may be substituted one of the other well-known catalytic polymerizations at 150-310°, using $H_3PO_4$ , $AlCl_3$ , $Al_2O_3$ , $SiO_2$ , $NaAlCl_4$ , $H_2SO_4$ .		Process Management Co., Inc. (Atwell); U.S.P. 2,145,576, Jan. 31, 1939.

Table 6 (Continued).

Reaction	Catalyst	Observer
Polymerization of olefins, especially mixtures containing propylene, isobutylene, and pentene to benzene and higher hydrocarbons; T. 80-120°; pressure 1-10 atm.; during polymerization as much water may be added as is removed by the reaction products; the catalyst may be regenerated by a timely heating to 200°; instead of olefins the corresponding alcohols may be used; from the reaction products the alcohols formed are separated and returned to the polymerization zone.	Solid carriers (charcoal, pumice, majolica fragments, asbestos, silica gel, lime rings) covered or impregnated with aqueous H <sub>2</sub> SO <sub>4</sub> (40-70%) or with acid-reacting sulfates [(NaHSO <sub>4</sub> ), Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , CuSO <sub>4</sub> ], as well as sulfates + H <sub>2</sub> SO <sub>4</sub> ], or with sulfonic acids (of benzene, naphthalene) or with ethyl sulfuric acid; the acid may be used with the addition of H <sub>3</sub> PO <sub>4</sub> or soot.	N. V. de Bataafsche Petroleum Mij: F.P. 836,721, Jan. 25, 1939.
Polymerization of gaseous olefins; a mixture of cracking benzene and gaseous hydrocarbons obtained by cracking is subjected to treatment over fuller's earth or silica gel; T. 205-365°; pressure, 7-52 atm.; thereby polymerization of unsaturated resin-formers takes place; the benzene is separated from the resin-free product, and the gaseous parts still containing the unsaturated hydrocarbons are polymerized with solid H <sub>3</sub> PO <sub>4</sub> acid catalyst to liquid hydrocarbons, especially benzene; T. 150-310°; pressure 4-35 atm.; the polymer benzene may be added to the first refining stage; by pretreatment the damaging of the polymerization catalyst by resin-formers is avoided.	AlCl <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> , or H <sub>3</sub> PO <sub>4</sub> .	Texas Company (Story): U.S.P. 2,142,969, Jan. 3, 1939.
Polymerization of olefinic hydrocarbons; dimerization of cyclopentadiene; catalyzed dimerization of trimethylethylene and polymerization of symmetrical methylethyl ethylene, $\beta$ -butylene, isobutylene, propylene, butadiene and binary mixtures of these are investigated.	CuS, Cu <sub>2</sub> S, Ag <sub>2</sub> S, SrS, ZnS, CdS, HgS, Ti <sub>2</sub> S, SnS <sub>2</sub> , SnS, PbS, As <sub>2</sub> S <sub>3</sub> , Bi <sub>2</sub> S <sub>3</sub> , MoS <sub>2</sub> , FeS, FeS <sub>2</sub> , KFeS <sub>2</sub> , CuFeS <sub>2</sub> and NiS (most black sulfides are catalytically active, while the white and yellow sulfides appear to be inactive; most active is CuS).	Ingold and Wassermann: <i>Trans. Faraday Soc.</i> , <b>35</b> , 1022-24 (1939).
Polymerization of olefins (in the liquid phase); good yields of dimer polymerizates and small amounts of higher polymers are formed, e.g., isobutylene is polymerized at about 110° and 60 atm. to a product containing 73% diisobutylene, 23% triisobutylene and only 3% of higher polymers; from a mixture of isohexylene and isohexylene (from alcohols, water gas obtained by dehydrogenation) was obtained a polymerizate (96%) at 39° which contained 91% of dimers.	H <sub>2</sub> SO <sub>4</sub> or H <sub>3</sub> PO <sub>4</sub> .	I. G. Farbenindustrie A.-G. F.P. 844,022 (1939).
Depolymerization of unsaturated high-boiling hydrocarbons; volatile polymer olefins are depolymerized in the presence of considerable amounts of water, e.g., the trimer, obtained besides the dimer by treating isobutylene with acids, such as H <sub>3</sub> PO <sub>4</sub> or H <sub>2</sub> SO <sub>4</sub> , is led over the catalyst at 230° in a ratio of 58% of the trimer to 42% of water vapor.	Tonsil.	I. G. Farbenindustrie A.-G.: F.P. 842,821, June 20, 1939.
Deparaffination of mineral oils by addition of small amounts of substances obtained from cracking residues by polymerization below 260° and long time of polymerization, or short time of polymerization above 260°; before separating the catalyst sludge the mass is heated to 370° at which cracking starts; then the sludge is separated and distilled in vacuum to avoid cracking; the remaining solid residue is used as a helping agent for the removal of paraffin from mineral oils.	Small amount AlCl <sub>3</sub> (2-5%). Large amount of AlCl <sub>3</sub> (5-10%).	Standard Oil Development Co.: F.P. 840,392, April 25, 1939.

Table 7. Catalytic Hydropolymerization of Olefins.

Reaction	Catalyst	Observer
Polymerization and hydrogenation of $C_3H_6$ ; ethylene decomposes and polymerizes and a mixture of ethylene and $H_2$ reacts to form ethane by the action of resonated atoms; the rate of ethane formation is proportional to the square root of the $H_2$ pressure.	Excited Hg atoms.	Olson and Meyers: <i>J. Am. Chem. Soc.</i> , <b>48</b> , 389 (1926).
Hydro- and dehydropolymerization of olefinic hydrocarbons, such as isobutylene: (1) $HOSO_2OC_4H_9 + C_4H_8 \rightarrow H_2SO_4 + C_4H_{10}$ (2) $HOSO_2OC_4H_9 + C_4H_{10} \rightarrow HOSO_2OC_4H_7 + C_4H_8$ (3) $nHOSO_2OC_4H_7 \rightarrow nH_2SO_4 + (C_4H_8)_n$ .	$H_2SO_4$ , $AlCl_3$ (less desirable due to greater complexity through simultaneous cracking reactions).	Nametkin, Abakumovskaja and Rudenko: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>7</b> (69), 759-762 (1937).
Hydropolymerization of isobutylene to isooctane and amylene and then to isodecane; T. 275° pressure, 80 atm.; time, 4 hrs.	$NiO + ZnCl_2$ or $AlCl_3$ ; $H_3PO_4 + NiO + Fe$ catalyst; 10 p. reduced $Fe + 2$ p. $MgCl_2 \cdot 6H_2O$ ; hydrogenation catalyst + polymerization catalysts such as $MgCl_2$ , $ZnCl_2$ , $AlCl_3$ .	Ipatieff and Komarewsky: <i>Ind. Eng. Chem.</i> , <b>29</b> , 958-959 (1937). Ipatieff and Komarewsky: U.S.P. 1,993,512 (1937). Ipatieff and Komarewsky: <i>J. Am. Chem. Soc.</i> , <b>59</b> , 720-722 (1937).
Simultaneous polymerization and hydrogenation of olefins: 100 parts of isobutylene; T. 275°; pressure, 100 atm. $H_2$ (initial pressure, 75 atm. $H_2$ ); time, 12 hrs.; yield, 50% isooctane.	2.5 p. Mo oxide, 70.0 p. $H_4P_2O_7$ , 30.0 p. kieselguhr at 150° mixed to a paste, heated for 20 hrs. at 275° and evaporated to dryness; pieces 1.6-4 mesh/cm. in size.	Universal Oil Products Company: F.P. 821,136, Nov. 27, 1937.
Simultaneous polymerization and hydrogenation of olefins: 100 p. of isobutylene are heated over 2.5 p. Mo oxide and 1 p. $ZnCl_2$ for 12 hrs. at 275° under 100 atm. $H_2$ pressure.	(1) Polymerization catalysts: $AlCl_3$ , $ZnCl_2$ , $MgCl_2$ , $H_2SO_4$ , $H_3PO_4$ , $HClO_4$ , $BF_3$ in the presence of (2) Hydrogenating catalysts: oxides or sulfides of metals of the left part of the 6th group: Mo oxide.	Universal Oil Products Company: F.P. 820,579, Nov. 15, 1937.
Simultaneous polymerization and hydrogenation of olefins to form hydrocarbons of high C content, e.g., mixtures of gaseous propylene and butylene give 30-50% benzene consisting of isohexane, isooctane and isodecane; from isobutylene, in one step, is obtained 50% isooctane (2,2,4-trimethylpentane); T. 275°; pressure, 100 atm.	$AlCl_3$ , $ZnCl_2$ , $MgCl_2$ , $HClO_4$ , $H_2SO_4$ , $H_3PO_4$ , $BF_3$ ; oxides or sulfides of the 6th or 8th group of the periodic system, especially $H_3PO_4$ on kieselguhr.	Universal Oil Products Co. (Ipatieff and Komarewsky): Austrian P. 103,401, March 31, 1938.

Table 8. Catalytic Polymerization of Isoprene.

Reaction	Catalyst	Observer
Polymerization of isoprene.	Microorganisms present in natural rubber and in latex.	Badische Anilin- und Soda Fabrik (Wallace): E.P. 15,299 (1909).
Polymerization of isoprene to rubber-like substances.	$CeSO_4$ , blue V salts or oxidizable metals.	Badische Anilin- und Soda Fabrik: F.P. 440,173 (1910).
Polymerization of isoprene.	Peptones, albumins, keratins.	Heinemann: F.P. 439,101 (1910).
Polymerization of isoprene.	Electrical energy.	The Bayer Company: F.P. 432,222 (1910).
Polymerization of isoprene in a sealed tube.	$CH_3COOH$ .	The Bayer Company: E.P. 15,254 (1910). Harries: <i>Z. angew. Chem.</i> , <b>25</b> , 1457 (1912).
Polymerization of isoprene.	Alkalies.	Badische Anilin- und Soda Fabrik: F.P. 417,170 (1910).
Polymerization of isoprene.	Amides, nitrides, alkaline earths.	The Bayer Company: E.P. 1,125 (1911).
Polymerization of isoprene.	Urea, blood, fibrin.	The Bayer Company: E.P. 1,124 (1911).

Table 8 (Continued).

Reaction	Catalyst	Observer
Polymerization of isoprene.	Heat, followed by acid treatment; O <sub>2</sub> or O <sub>3</sub> ; ultraviolet light or x-rays; anhydrides of organic acids; organic or inorganic acids; traces of S.	Badische Anilin- und Soda Fabrik: F.P. 434,587 (1911).
Polymerization of isoprene to rubber.	A small amount of Na or Na amalgam, either cold or moderately heated.	Harries: <i>Ann.</i> , <b>157</b> , 383 (1911). Matthews: E.P. 24,790 (1910).
Polymerization of isoprene, butadiene, dimethyl butadiene to rubber.	Oxidizing agents, such as O <sub>2</sub> or O <sub>3</sub> , or substances producing them.	I. G. Farbenindustrie A.-G.: E.P. 286, 272, March 2, 1927.
Polymerization of isoprene to rubber; T. 50–70°C.	Soap (either as emulsifying agent or as catalyst).	Dinsmore: U.S.P. 1,732,795, Oct. 22, 1929.
Polymerization of isoprene (when freshly distilled, polymerizes more slowly than when kept for a few days in an atmosphere of N containing a small amount of O <sub>2</sub> ); partial polymerization effected at 12,000 atm. pressure in the absence of O <sub>2</sub> (autocatalytic); the polymerized product obtained is a rubber-like solid.	Shaking with O <sub>2</sub> or mixing with a small amount of pinene (which has been shaken with O <sub>2</sub> ) accelerates the reaction; quinol acts as a negative catalyst.	Conant and Tongberg: <i>J. Am. Chem. Soc.</i> , <b>52</b> , 1659 (1930). Bridgman and Conant: (Refer to C. 1929 1243).
Polymerization of isoprene and butadiene to synthetic rubber.	Na.	Harries: I.G. Farbenindustrie A.-G.: E.P. 339,243 (1930). E.P. 337,460 (1930). E.P. 338,534 (1930).
Polymerization of isoprene.	The addition of NaCl and Na <sub>2</sub> SO <sub>4</sub> is recommended.	I.G. Farbenindustrie A.-G.: F.P. 687,773 (1930). F.P. 687,808 (1930).
Polymerization of isoprene.	Dioxane, simple ethers.	I. G. Farbenindustrie A.-G.: E.P. 334,184 (1930).
Polymerization of isoprene.	Unsaturated ethers, S derivatives.	I. G. Farbenindustrie A.-G.: E.P. 340,474 (1930). F.P. 695,299 (1930).
Polymerization of isoprene.	Thiophene, oxides of olefins.	I.G. Farbenindustrie A.-G.: E.P. 308,755 (1929).
Polymerization of isoprene to an amorphous compound which decomposes at 190° and melts at 130°.	TiCl <sub>4</sub> in CHCl <sub>3</sub> ; SnCl <sub>4</sub> (the polymeride obtained with this catalyst is dehydrogenated by Se to 1,2,5-trimethyl naphthalene at 280–340°).	Wagner-Jauregg: <i>Ann.</i> , <b>496</b> , 52–77 (1932).
Polymerization of isoprene to polymers of various molecular weights.	Olefins: 2-pentene + AlCl <sub>3</sub> .	Thomas and Carmody: <i>J. Am. Chem. Soc.</i> , <b>53</b> , 3854 (1933).
Polymerization of isoprene with pentene, forming an insoluble gelatinous polymer; HCl accelerates the reaction and favors the formation of soluble polymers; the action of pentene upon the polymerization of isoprene is due to the activity of the solvent.	AlCl <sub>3</sub> ; HCl; care must be taken that the AlCl <sub>3</sub> -pentane complex is always dissolved; isoprene acts similarly, particularly the hydrochloride or the ethyl acetate which causes AlCl <sub>3</sub> to dissolve in isoprene.	Thomas and Carmody: <i>J. Am. Chem. Soc.</i> , <b>55</b> , 3854–3856 (1933).
Polymerization of isoprene in vapor phase to soluble polymers; T. 24–26°; duration of experiment, 1,000 hrs.	AlCl <sub>3</sub> .	Carmody, W. H. and Carmody, M. O.: <i>Ibid.</i> , <b>59</b> , 2073–2074 (1937).
Polymerization of isoprene; pressure, 2000 atm. or more; with or without heat and catalysts; the organic cpds. may be used alone or in a mixture, as a solution or as an emulsion, e.g., treatment of isoprene, 2,3-dimethyl butadiene, styrene and styrene-malonic ester.		Imperial Chemical Industries, Ltd.: E.P. 365,102, May 7, 1929.

Table 9 Catalytic Polymerization of Butadiene.

Reaction	Catalyst	Observer
Polymerization of butadiene.	Acetic anhydride or $\text{H} \cdot \text{COOH}$ .	Shering-Kahlbaum A.-G.: F.P. 439,101 (1909).
Polymerization of butadiene to rubber.	A small amount of finely dispersed colloid (soluble heavy metal oxides which do not develop $\text{H}_2\text{O}_2$ with acids).	I. G. Farbenindustrie A.-G.: G.P. 515,143, July 21, 1927.
Polymerization of butadiene with a substance which emulsifies; reaction proceeds slowly.	Na oleate + 2% casein which acts as a protective colloid.	Goodyear Tire & Rubber Co.: E.P. 297,050 (1928).
Polymerization of butadiene in two stages: (1) to a higher density; (2) continuing with.	(1) Na; (2) other polymerization catalysts.	I. G. Farbenindustrie A.-G.: E.P. 307,308, June 4, 1929.
Polymerization of butadiene.	A mixture of K and Na.	General Motors Corporation: U.S.P. 1,713,286 (1929).
Polymerization of butadiene emulsified with alizarine oil; the emulsion is kept for 14-20 days in an autoclave at 60-90° whereby polymerization takes place.	$\text{Na}_3\text{PO}_4$ or Mg oleate; Na salt of isobutyl sulfuric acid; $\text{NH}_4$ oleate.	I. G. Farbenindustrie A.-G.: P.P. 646,704 (1929). E.P. 301,515 (1929).
Polymerization of butadiene to polymers soluble in organic solvents.	Nitrogen bases, hydrazine derivatives, or their salts.	Schmidt and von Bock: G.P. 504,436, March 22, 1929.
Polymerization of butadiene to rubber in the presence of phenols which prevent the formation of difficultly soluble products.	Oxidizing agents.	I. G. Farbenindustrie A.-G.: F.P. 686,934, Dec. 19, 1929.
Polymerization of butadiene in the presence of halogenated organic cpds. to rubber.	Alkali and/or alkaline earths.	I. G. Farbenindustrie A.-G.: F.P. 702,784, Sept. 30, 1930. E.P. 347,802, Feb. 28, 1930.
Polymerization of butadiene.	Ni, Fe, or Co carbonyls.	I. G. Farbenindustrie A.-G.: E.P. 340,004 (1930).
Polymerization of butadiene.	Na stearate.	I. G. Farbenindustrie A.-G.: F.P. 690,484 (1931).
Polymerization of butadiene.	Albumin with Na stearate.	I. G. Farbenindustrie A.-G.: E.P. 294,693 (1928).
Polymerization of butadiene.	Na oleate.	I. G. Farbenindustrie A.-G.: E.P. 307,938 (1929).
Polymerization of butadiene formed by the pyrolysis of petroleum fractions (used in the synthetic rubber industry); T. 100°; pressure, 18-20 atm.; with stirring.	Diazoaminobenzene.	Lure and Igssatyuk: <i>Sintet. Kauchuk</i> (U.S.S.R.), 3, 12-14 (1932).
Polymerization of butadiene formed by the pyrolysis of $\text{EtOH}$ ; T. 50-60°; pressure, 4 atm.	Na metal.	
Polymerization of butadiene to solid polymers; T. 10-15°; time, 2-36 hrs.	Highly dispersed Na metal; colloidal solution of Na (0.001-0.01%).	Selmanow and Schalnikow: <i>Zhur. Fiz. Khim.</i> (U.S.S.R.), 4, 353-366 (1933).
Polymerization of butadiene to rubber emulsions.	Nitrogen bases and their salts.	von Bock and Tschunker: U.S.P. 1,924,227, Aug. 29, 1933.
Polymerization of butadiene at room temp.; reaction completed after 2 hrs.; condensed at 180°; after 25 hrs. at -68°; after 48 hrs. at 0°.	Na layers; crystalline effects account for the changes in activity.	Dankov: <i>Zhur. Fiz. Khim.</i> (U.S.S.R.), 4, 326-333 (1933).
Polymerization of butadiene.	Alkali or alkaline earth metals and a small proportion of a halogen derivative of a hydrocarbon, such as ethylene chloride, which serves to promote a quiet and uniform polymerization.	I. G. Farbenindustrie A.-G. (Ebert, Fries and Gartsch): U.S.P. 1,921,867, Aug. 8, 1933.

Table 9 (Continued).

Reaction	Catalyst	Observer
Polymerization of butadiene.	Organo-metallic cpds.	Ziegler, Dersch and Wollthan: <i>Ann.</i> , 511, 13 (1934). Ziegler and Jacob: <i>Ann.</i> , 511, 45 (1934).
Polymerization of butadiene to liquid polymers.	Na (0.5-1.0% Na in 4 days).	Andreev, Makashina and Maltzeva: <i>Sintet. Kauchuk (U.S.S.R.)</i> , 3 (1932).
Polymerization of butadiene.	Rubber tree extract.	Gibbons: U.S.P. 1,953,169, April 3, 1934.
Polymerization of monochlor-1,3-butadiene.	H <sub>2</sub> O.	Starkweather: U.S.P. 1,950,437, Mar. 13, 1934.
Polymerization of butadiene in the presence of ethylene acetal.	Alkali metals.	I. G. Farbenindustrie A.-G. (Ebert and Gartsch): U.S.P. 1,953,468, April 3, 1934.
Polymerization of butadiene (80%) to rubber and other polymers at room temp.	Na.	Koblyanski and Ivanova: <i>Sintet. Kauchuk (U.S.S.R.)</i> , 4, 11 (1935).
Polymerization of butadiene to rubber.	Na (0.5%).	Lebedev: <i>Chimie &amp; industrie</i> , 32, 1150 (1935).
Polymerization of butadiene (78%).	Na + Fe <sub>2</sub> O <sub>3</sub> or MgO.	Kravetz: <i>Sintet. Kauchuk (U.S.S.R.)</i> , 4, 36 (1935).
Polymerization of butadiene to rubber (80-90%); a chain reaction polymerization, a linear function of time: $M = a + bT$ ; the physical properties of rubber increase with a decrease in polymerization velocity; velocity constant: $K = 1/O \cdot \log x/a - x$ , where O is time (from the moment of highest velocity of the reaction) and x, yield of rubber (from the moment of highest velocity of the reaction multiplied by 2).	Diazoaminobenzene (1.5-2.0%) in the form of an emulsion showed catalytic action similar to peroxides; Cu-Zn and Ni salts slow down or prevent polymerization at conc. of the coagulation threshold; nitrophenol and azoxybenzene act non-catalytically.	Balandina, Beresau, Dogadkin and Lapuk: <i>Izvest. Akad. Nauk U.S.S.R.</i> , 423-435 (1936).
Polymerization of butadiene.	Finely divided catalysts acting by the use of hollow spaces such as those formed by the fast motion of liquids in a turbine.	I. G. Farbenindustrie A.-G.: F.P. 819,095, Oct. 9, 1937.
Polymerization of cyclopentadiene.	SnCl <sub>4</sub> , TiCl <sub>4</sub> , Sb <sub>2</sub> Cl <sub>5</sub> or cpds. exhibiting auxiliary valence.	Staudinger and Bruson: <i>Ann.</i> , 447, 97, 110 (1938).
Polymerization of dienes, e.g., liquid butadiene, which is treated with anhydrous HCl or HBr at low temp., e.g., -60° or under pressure whereby, depending on the duration of polymerization, viscous oils are obtained, which dry in air and serve as substitutes for linseed oil, wood oil, or rubber-like polymerizates; a longer duration of polymerization brings about horny products; the polymerizate is separated from the monomer by distilling off the latter or precipitating with methanol; in a similar way, isoprene may be converted, or a mixture of butadiene, n-butylene and propylene obtained by dechlorination of dichlorobutane.	Metal halides or per-acid salts and H <sub>2</sub> O <sub>2</sub> accelerate the reaction.	I. G. Farbenindustrie A.-G.: F.P. 835,373, Dec. 20, 1938.

Table 10. Catalytic Polymerization of Diolefins.

Reaction	Catalyst	Observer
Polymerization of diolefins to rubber.	Polymerized castor oil through which an oxidizing gas has been passed.	I. G. Farbenindustrie A.-G.: E.P. 322,114, Dec. 17, 1928.
Polymerization of diolefins to rubber.	H <sub>2</sub> SO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub> , sulfonic acid and sulfonyl chlorides.	I. G. Farbenindustrie A.-G.: E.P. 338,152, May 14, 1929.
Polymerization of diolefins to rubber.	Peroxides, H <sub>2</sub> plus urea, KF <sub>3</sub> , sodium acetate.	I. G. Farbenindustrie A.-G.: E.P. 318,115, April 26, 1928.
Polymerization of diolefins to rubber emulsion.	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> .	I. G. Farbenindustrie A.-G.: E.P. 312,949, Jan. 2, 1928.
Polymerization of diolefins to rubber; T. 10-20°C.	H <sub>2</sub> O <sub>2</sub> in the presence of Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> · 2H <sub>2</sub> O.	I. G. Farbenindustrie A.-G.: E.P. 364,089, Aug. 21, 1930. Luther and Henck: U.S.P. 1,860,681, May 31, 1932.

Table 10 (Continued).

Reaction	Catalyst	Observer
Polymerization of diolefins to rubber.	Alkali or alkaline-earth metals.	I. G. Farbenindustrie A.-G.: E.P. 363,810, Dec. 11, 1930.
Polymerization of diolefins.	Bleaching earth.	Sinclair Refining Company: U.S.P. 1,797,255 (1931).
Polymerization of diolefins.	Described as a method; no mention made of catalysts.	Shestkow: Russ. P. 38,777, Sept. 30, 1934.
Selective polymerization of diolefins; T. 200–300°.	Active charcoal or silica gel.	I. G. Farbenindustrie A.-G. (Zobel and Reich): G.P. 630,249 (1936). F.P. 716,882 (1931).
Selective polymerization of isoolefins; T. 50–150°; atmospheric pressure; T. up to 250°; pressure, 4–7 atm.	Al <sub>2</sub> O <sub>3</sub> on charcoal or H <sub>3</sub> PO <sub>4</sub> on kieselguhr or Cd on silica gel.	Standard Oil Development Co.: F.P. 806,886 (1937).

Table 11. Catalytic Polymerization of Vinyl Compounds.

Reaction	Catalyst	Observer
Polymerization of vinyl cpds.; T. 40°C.	Benzoyl or acetyl peroxide.	Shriver: E.P. 397,314, Aug. 24, 1933.
Polymerization of vinyl cpds., particularly vinyl chloride or vinyl acetate.	Benzoyl or acetyl peroxide.	Carbide and Carbon Chemicals Corporation: F.P. 748,972, July 13, 1933.
Polymerization of vinyl cpds. which, together with an organic acid anhydride and a true salt, react in the presence of a solvent in which the catalytic reaction product is soluble, and the non-catalytic product insoluble; separation of catalyst solution from the undissolved by-products may occur, e.g., Ac <sub>2</sub> O in toluene and vinyl acetate containing AcH.	Na perborate.	
Polymerization of vinyl cpds. to plastic products of low solubility in water and organic solvents.	HCl acid.	Voss: G.P. 578,996, Sept. 25, 1933.
Polymerization of vinyl cpds.; pressure, less than 30 atms.	Ozone.	I. G. Farbenindustrie A.-G.: E.P. 410,132, May 7, 1934.
Polymerization of vinyl cpds. to low polymers.	Benzoyl or acetyl peroxide plus a ferrous alloy.	Carbide and Carbon Chemicals Corporation: F.P. 782,836, June 12, 1935.
Polymerization of vinyl acetylene to higher polymers (oily, gelatinous, or resinous); T. less than 413°C.	Oxygen or air.	Nieuwland: U.S.P. 1,812,541, June 30, 1931.
Polymerization of vinyl acetylene in the presence of toluene to higher polymers (oily, gelatinous, or resinous).	Benzoyl peroxide.	Dupont: E.P. 385,963, Dec. 28, 1932.
Stabilization of vinyl cpds. and aromatic vinyl cpds., especially styrene, to prevent polymerization.	Polymerization is inhibited by Cu and Fe salts of salicylic acid (0.005–0.020 parts to 1 part of styrene).	Dow Chemical Co. (Stoesser): U.S.P. 2,154,389, April 11, 1939.
Polymerization of vinyl acetylene to polymers; T. 110°; pressure, 10–20 atms.; time, 6 hrs.; yield, 20–30%.	Benzoyl peroxide, 1%.	Carter and Downing: U.S.P. 1,896,162, Feb. 7, 1933.
Polymerization of vinyl acetylene; T. 50–110°C.	AlCl <sub>3</sub> (less than 2%), arsenic chloride, boron fluoride.	Carter and Downing: U.S.P. 1,896,162, Feb. 7, 1933.
Polymerization of vinyl acetylene; T. greater than 80°.	Cu cpds. containing NH <sub>4</sub> , K, Na, Ca chlorides, sulfates or phosphates on carriers, such as charcoal, bleaching earth, kieselguhr.	I. G. Farbenindustrie A.-G.: F.P. 798,309 (1936).
Polymerization of vinyl acetate and vinyl chloracetate.	Ozonides.	Klatte and Rollett: U.S.P. 1,241,738, Oct. 2, 19

Table 11 (Continued).

Reaction	Catalyst	Observer
Polymerization of vinyl acetate.	Aldehydes: acetaldehyde + $\text{CH}_3\text{COOH}$ and paraldehyde + $\text{KC}_2\text{H}_3\text{O}_2$ .	Konsortium für Elektrochemische Industrie: E.P. 261,406, Nov. 14, 1925.
Polymerization of vinyl acetate; reaction slower than that of isoprene.	Quinol, accelerates; oxidized pinene, a negative catalyst.	Conant and Tongberg: <i>J. Am. Chem. Soc.</i> , <b>52</b> , 1659 (1930).
Polymerization of vinyl acetate; T. 180°; in quartz vessels, more rapid in the presence of $\text{N}_2$ or $\text{CO}_2$ than in $\text{O}_2$ or air.	Oxygen, light.	Staudinger and Schwalbach: <i>Ann.</i> , <b>488</b> , 8-56 (1931).
Polymerization of vinyl acetate.	Inhibitor; ultraviolet light inhibits polymerization.	Taylor and Vernon: <i>J. Am. Chem. Soc.</i> , <b>53</b> , 2527 (1931).
Polymerization of vinyl acetate to a hard resin.	$\text{H}_2\text{O}_2$ in the presence of $\text{H}_2\text{O}$ and $\text{H}_2\text{CO}_3$ .	Scheidemandel: G.P. 615,995, July 17, 1935.
Polymerization of vinyl chloride or vinyl acetate; T. 40°C.	Benzoyl peroxide + Pb, Sn, or Al.	Young and Douglas: U.S.P. 2,011,132, Aug. 13, 1935.
Polymerization of vinyl chloride in sunlight.	Uranyl nitrate.	Flumiani: <i>Z. Elektroch.</i> , <b>32</b> , 271 (1926).
Polymerization of vinyl bromide; reaction complete; time, 20 hrs.	$\text{H}_2\text{O}_2$ .	Guyer and Schultze: <i>Helv. Chim. Acta</i> , <b>17</b> , 1544 (1935).
Polymerization of polyvinyl bromide to $(\text{C}_6\text{H}_5)_2$ ; T. 100-140°; the polymerized product is less unsaturated than rubber and resembles cyclo-rubber when treated with $\text{O}_3$ .	Dimethyl Zn in xylene.	Staudinger, Brunner and Feist: <i>Helv. Chim. Acta</i> , <b>13</b> , 805, 832 (1930).
Polymerization of polyvinyl bromide to $(\text{C}_6\text{H}_{10})_2$ ; T. 50-160°; the polymerized product is a mixture of long straight-chain cpds.; reduction with $\text{CH}_3\text{COOH}$ in HCl to $\text{C}_{12}\text{H}_{22}$ (b.p. 123-126°; $d_4^{20} = 0.8771$ ; soluble in acetone); T. 120-130°.	Diethyl Zn in xylene.  Zn dust in xylene.	
Polymerization of divinyl acetylene to a synthetic drying oil; T. 80-100°C.; time, 4 hrs.; yield, 12-18%.	Metals; Co and Co linoleate.	Collins: U.S.P. 1,869,668, Aug. 2, 1932.
Polymerization of divinyl.	Thin layers of Na metal obtained by condensation of Na vapors in vacuum; higher polymerization velocity than with Na pieces (ten times); not the increase in the surface, but the increase in chemical activity by dissolution of Na in divinyl is related to the degree of dispersion of the thin Na layer.	Dankow and Krasnobajewa: <i>Zhur. Fiz. Khim.</i> (U.S.S.R.), <b>4</b> , (1933).
Mixed polymerizate from $\beta, \beta'$ -dimethylacrylic acid vinyl ester, $(\text{CH}_3)_2\text{C}=\text{CH} \cdot \text{COOCH}=\text{CH}_2$ , or crotonic acid vinyl ester, $\text{CH}_3 \cdot \text{CH}=\text{CH} \cdot \text{COO} \cdot \text{CH}=\text{CH}_2$ , or isobutylene vinyl ketone, $(\text{CH}_3)_2\text{C}=\text{CH} \cdot \text{CO} \cdot \text{CH}=\text{CH}_2$ , and vinyl chloride, acetate, ethyl vinyl ether, styrene, methyl vinyl ketone, or ethyl vinyl ketone are prepared as emulsions or as solutions; the polymerizate obtained may be vulcanized in the ordinary manner. e.g., heated with S and ZnO and thereby converted into insoluble and non-thermoplastic substances, even when mixed with softeners.		I. G. Farbenindustrie A.-G.: E.P. 496,276, Dec. 22, 1938.



Table 11 (Continued).

Reaction	Catalyst	Observer
Polymerization of vinyl acetate in 17-40% toluene solution; T. 80°; there is always an induction interval; activation energy for the polymerization reaction is 17.2 k.cal./g.mol; viscosity and molecular weight measurements show chain length from 370 at $2.02 \cdot 10^{-2}$ mol/l. catalyst to 1560 at $3.3 \cdot 10^{-2}$ mol/l.; at higher temp., especially in the last stages of the reaction, chain branching takes place; toluene acts as energy transmitter; an activated solvent molecule either transfers its energy to a monomer while it incites a new chain, or loses its activity by reaction with a likewise activated solvent molecule.	Benzoyl peroxide (0.4% dissolved in toluene); activation energy for the decomposition of the catalyst is 29 k.cal./g.mol.	Cuthbertson, Gee and Rideal: <i>Proc. Roy. Soc. London (A)</i> , <b>170</b> , 300-322 (1939).

Table 12. Catalytic Polymerization of Acetylene.

Reaction	Catalyst	Observer
Polymerization of $C_2H_2$ to a heavy petroleum-like oil, cuprene; T. 225-250°C.	Cu.	Alexander: <i>Ber.</i> , <b>32</b> , 2381 (1899).
Polymerization of $C_2H_2$ to liquid, solid, and gaseous hydrocarbons; T. 200-250°C.	Ni.	Sabatier and Senderens: <i>Compt. rend.</i> , <b>128</b> , 1173 (1899); <b>130</b> , 1559 (1900); <b>131</b> , 187 (1900).
Polymerization of $C_2H_2$ to benzene, styrene and reduction products of naphthalene and anthracene; T. 150°.	Pt.	Sabatier and Senderens: <i>Bull. soc. chim.</i> (3), <b>25</b> , 678 (1901). Sabatier and Senderens: <i>Ann. chim. phys.</i> (8), <b>4</b> , 439 (1905). Egloff, Lowry and Schaad: "Polymerization and Decomposition of Acetylene Hydrocarbons," Universal Oil Products Company, Booklet No. 137.
Polymerization of $C_2H_2$ .	Cr sponge.	Horwitz: G.P. 205,700, Jan. 22, 1907.
Polymerization of $C_2H_2$ to aromatic liquids (57.8%), tars and gases; T. 440-1150°C.; time, 8½ hrs.	Porcelain.	Bone and Coward: <i>J. Chem. Soc.</i> , <b>93</b> , 1197 (1908).
Polymerization of $C_2H_2$ in the presence of $CH_4$ (50 : 50) to $C_2H_6$ .	Cu on pumice.	Heinemann: F.P. 458,397, May 27, 1913.
Polymerization of $C_2H_2$ to aromatic and aliphatic hydrocarbons.	Clays, bauxite.	Steur and Grob: E.P. 109,983, July 17, 1916.
Polymerization of $C_2H_2$ ; T. less than 500°C.	Glass.	Hilpert: <i>Ges. Abhandl. Kennniss Kohle</i> , <b>1</b> , 271 (1917).
Polymerization of $C_2H_2$ to products similar to cuprene; T. 200-400°C.	Fe + Mg.	N. V. Elektro-Zuurstofen Waterstofffabrika: E.P. 303,797 (1920). Dutch P. 20,851 (1929). (refer to C. 1930 I 2161.)
Polymerization of $C_2H_2$ to oils and gases; T. 600°C.	Boron.	Tiede and Jenisch: <i>Brennstoff-Chem.</i> , <b>2</b> , 5 (1921).
Polymerization of $C_2H_2$ ; T. 220-250°C.	$Cu_2Fe(CN)_6 \cdot 7H_2O$ .	Kaufmann and Schneider: <i>Ber.</i> , <b>55B</b> , 267 (1922).
Polymerization of $C_2H_2$ to "carbon" and $H_2$ ; T. 725°C.	Carbon.	Bradley and Parr: <i>Chem. Met. Eng.</i> , <b>29</b> , 737 (1922).
Polymerization of $C_2H_2$ to liquids and solids; T. less than 100°C.	Boron hydrides.	Stock and Kuss: <i>Ber.</i> , <b>56B</b> , 789 (1923).
Polymerization of $C_2H_2$ to aromatic liquid hydrocarbons (50% $C_6H_6$ ) without simultaneous formation of solid hydrocarbons; T. 600-650°.	Active birch and basswood.	Zelinsky and Kasansky: <i>Ber.</i> , <b>57</b> , 264 (1924).

Table 12 (Continued).

Reaction	Catalyst	Observer
Polymerization of $C_2H_2$ ; T. less than $480^\circ C$ .	$H_3PO_4$ .	Bahr: <i>Ges. Abhandl. Kenntnis Kohle</i> , <b>8</b> , 283 (1924).
Polymerization of $C_2H_2$ .	Ions of inert gases: nitrogen, helium, xenon and krypton; ionization potential does not control the catalytic effect; gases ionized by $\alpha$ -radiation.	Lind and Bardwell: <i>J. Am. Chem. Soc.</i> , <b>48</b> , 1577 (1926).
Polymerization of $C_2H_2$ to acetylene tar; T. $400$ – $700^\circ$ ; yield, 82%; rate, 5 l./hour at $650^\circ$ ; tar fraction (b.p. below $175^\circ$ ) consists of benzene and other aromatic hydrocarbons; tar fraction (b.p. $175$ – $250^\circ$ ) consists essentially of naphthalene; yield of gas oil fraction greatest with charcoal as catalyst.	Charcoal or Japanese acid earth; porcelain and glass tubes act similarly in the polymerization of $C_2H_2$ ; products of $C_2H_2$ decomposed in a metal tube (C, $H_2$ , and gaseous substances) more abundant than polymerization products.	Fujio: <i>J. Soc. Chem. Ind. Japan (Suppl.)</i> , <b>31</b> , 77–86 (1928).
Polymerization of $C_2H_2$ .	Carbon.	Constable: <i>Nature</i> , <b>122</b> , 882 (1928).
Polymerization of $C_2H_2$ .	Porcelain tube filled with kieselguhr or active charcoal.	Fischer: <i>Brennstoff-Chem.</i> , <b>10</b> , 279 (1929).
Polymerization of $C_2H_2$ ; T. less than $300^\circ C$ .	Ni.	Fukagawa: <i>J. Chem. Soc. Japan</i> , <b>50</b> , 689 (1929).
Polymerization of $C_2H_2$ or its homologs in the presence of steam to cyclic hydrocarbons; T. $250$ – $500^\circ C$ .	ZnO or silica gel.	I. G. Farbenindustrie A.-G.: E.P. 334,203, Feb. 23, 1929.
Polymerization of $C_2H_2$ .	Graphite catalysts which cause a simultaneous precipitation of carbon (catalyst deformed in this manner also favors the polymerization of other hydrocarbons).	Krauch: <i>Petroleum Age</i> , <b>25</b> , 699–706 (1930).
Polymerization of $C_2H_2$ pressure, less than 30 cm.	Light (wave length, $2,537 \text{ \AA}$ ), inactive; quantum efficiency, for shorter wave lengths, about $7.4 \pm 2.5$ .	Lind and Livingston: <i>J. Am. Chem. Soc.</i> , <b>52</b> , 4613 (1930).
Polymerization of $C_2H_2$ to gaseous and liquid polymers; T. $580^\circ C$ .	Ca phosphate.	Berl and Hoffmann: <i>Z. angew. Chem.</i> , <b>44</b> , 259 (1931).
Polymerization of $C_2H_2$ to vinyl acetylene, divinyl acetylene and a tetrameride.	An aged mixture of $Cu_2Cl_2$ , $NH_4Cl$ , Cu and aqueous HCl.	Nieuwland, Calcott, Downing and Carter: <i>J. Am. Chem. Soc.</i> , <b>53</b> , 4197 (1931).
Polymerization of $C_2H_2$ to butadiene, benzene, toluene, naphthalene; T. $420$ – $430^\circ$ ; gaseous products obtained: 32% $C_2H_2$ , 2% iso-olefins, 10% $n$ -olefins, 12% $H_2$ , 4% $CH_4$ , etc.; unsaturated hydrocarbons identified: ethylene, propylene, allene, propinene, butadiene; from 600 liters $C_2H_2$ , 190 g. liquid condensate obtained containing a small amount of olefins, benzene, PhMe, $C_{10}H_8$ , but no paraffins or naphthenes; formation of $C_6H_6$ in two stages: (1) two molecules $C_2H_2$ combine to form divinyl; (2) two molecules $C_2H_2$ unite to form benzene; propinene may be formed from propylene, which gives rise to allene.	5% $ZnCl_2$ + pumice.	Lozovoy: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>1</b> , 717 (1931).
Polymerization of $C_2H_2$ and olefins to benzene.	Al.	Ruhrchemie A.-G.: E.P. 324,422, May 26, 1932. Ipatieff and Klujkvin: <i>Zhur. Khim. Prom. (U.S.S.R.)</i> , <b>3</b> , 5 (1925). Ipatieff and Klujkvin: <i>Ber.</i> , <b>58B</b> , 4 (1925).
Polymerization of $C_2H_2$ .	Pt ( $150^\circ$ ); $AlCl_3$ ( $AlCl_3 \cdot C_2H_2$ cpd. formed).	Dupont (Calcott and Downing): U.S.P. 1,924,979, Aug. 29, 1933.
Polymerization of $C_2H_2$ .	$Al_2Cl_6 \cdot Et_2O \cdot C_2H_2$ or $Al_2Cl_6 \cdot 2PhNMe_2$ did not catalyze the reaction, either at room temp. or at $100^\circ$ ; argon (60% activity).	Rosenblum: <i>J. Phys. Chem.</i> , <b>38</b> , 683–688 (1934).
Polymerization of $C_2H_2$ to aromatic liquids; T. $300$ – $500^\circ C$ ; pressure, 10–200 atm.	Fe; Mg bromide contained in oil; Decalin.	N. V. de Bataafsche Petroleum Mij: Dutch P. 29,103, March 15, 1933.

Table 12 (Continued).

Reaction	Catalyst	Observer
Polymerization of $C_2H_2$ to vinyl acetylene.	$CuCl + NH_4Cl$ or an alkaline earth chloride.	Perkins and Tovissaint: U.S.P. 1,971,656, Aug. 28, 1934. Nieuwland: U.S.P. 1,811,959, June 30, 1931. F.P. 733,662, June 19, 1931.
Polymerization of $C_2H_2$ to benzene; T. 650°C.	Charcoal.	Clemo and McQuillen: <i>J. Chem. Soc.</i> , 1935, 851.
Polymerization of $C_2H_2$ by Hg vapor.	Ultraviolet light.	Toul: <i>Collection Czechoslovak Chem. Commun.</i> , 7, 491-493 (1935).
Polymerization of $C_2H_2$ to $6CuCl \cdot 3NH_4Cl \cdot C_2H_2$ .	18% $Cu_2Cl_2 + 20\% NH_4Cl$ .	Zürich and Ginsburg: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , 5 (67), 1468-1478 (1935).
Polymerization of $C_2H_2$ .	Au, Ag or Mo precipitated on active charcoal or silica gel.	Ammonia Casale Société Anonyme: F.P. 797,935 (1936).
Polymerization of $C_2H_2$ with olefins and $SO_2$ to polysulfones.	Ascaridol, as well as other peroxides.	Ryden, Glavis and Marvel: <i>J. Am. Chem. Soc.</i> , 59, 1014-1015 (1937).
Polymerization of $C_2H_2$ (33½%) in the presence of $H_2$ (66½%) to liquids: ethane, ethylene; 74.3% of liquid polymers.	Fe + Ni (9 : 1).	
Polymerization of $C_2H_2$ to motor fuel; T. 700°C.; any pressure.	Te on pumice.	

Table 13. Catalytic Polymerization of Styrene.

Reaction	Catalyst	Observer
Polymerization of styrene to polymers.	K phosphates, $H_2O$ .	Plauson: U.S.P. 1,436,819, Nov. 28, 1923.
Polymerization of styrene; T. 175-180°; time, 1.0-1.5 hrs.	Benzoyl peroxide.	Ostromislensky: U.S.P. 1,683,404, Sept. 4, 1928.
Polymerization of styrene; T. 110°C.; reaction effected by energy liberated during formation of initial oxidation products with unoxidized styrene molecules, as well as in subsequent reaction.	Benzoyl peroxide; the addition of anthracene increases the oxidation of styrene, but inhibits polymerization; also strongly inhibits the oxidation of benzaldehyde formed by the oxidation of styrene.	Milas: <i>Proc. Natl. Acad. Sci. U.S.</i> , 14, 844 (1928).
Polymerization of styrene.	Metals, alkalis.	Ziegler and Bahr: <i>Ber.</i> , 61B, 253 (1928).
Polymerization of styrene to polystyrenes; reaction very slow in the cold; velocity increases with increase in temp. to 250°; above 300°, depolymerization takes place.	$SnCl_4$ or other halides.	Staudinger, Brunner, Frey, Garbsch, Signer and Wehrli: <i>Ber.</i> , 62B, 24-26 (1929).
Polymerization of styrene in the cold to highly viscous, glass-like solutions.		Staudinger: <i>Z. angew. Chem.</i> , 42, 69 (1929).
Polymerization of styrene at high temp. to porous, powder-like polymer products and a slightly viscous solution.	$SnCl_4$ .	
Polymerization of styrene.	Oxygen.	I. G. Farbenindustrie A.-G.: E.P. 355,573, Jan. 28, 1930.
Polymerization of styrene to nonfriable polymers.	Alkali salts.	Naugatuck Chemical Co.: F.P. 695,575, May 14, 1930.
Polymerization of styrene by ultraviolet light to styrene polymer.	Oxygen.	Taylor and Vernon: <i>J. Am. Chem. Soc.</i> , 53, 2527 (1931).
Polymerization of styrene.	Benzoyl peroxide.	Natelson: <i>Ind. Eng. Chem.</i> , 25, 1391 (1933).

Table 13 (Continued).

Reaction	Catalyst	Observer
Polymerization of styrene in a solvent, such as methanol or ethylene chloride.	Ozone.	Lawson: U.S.P. 1,890,060, Dec. 6, 1933.
Polymerization of styrene with indene to gums.	Mercaptans.	Ward, Jordan and Fulweiler: <i>Ind. Eng. Chem.</i> , 24, 1238 (1932).
Polymerization of styrene; also of benzal acetone, dibenzal acetone, crotonal acetone, 2,4-hexadiene, Et sorbate and 1,3-cyclohexadiene.	Ozonides; on standing a decided decrease in activity takes place, indicating that the ozonide itself and not its decomposition products acts as catalyst; certain peroxides, and especially diisobutylene; ozonide more active catalyst than $O_3$ .	Houtz and Adkins: <i>J. Am. Chem. Soc.</i> , 53, 1058-1063 (1931); 55, 1609 (1933).
Polymerization of styrene in $CCl_4$ solution; T. 25-45°; polymerization velocity reproducible with freshly distilled styrene and is not changed by the addition of benzoyl peroxide.	$SnCl_4$ .	Williams: <i>J. Chem. Soc.</i> , 1938, 246-253.
Polymerization of styrene; the velocity of the primary reaction: $V_A = K_A G_{cat} C_{cat} (1 + G_{cat})$ , where $K_A$ = reaction constant; $c_{cat}$ and $C_{cat}$ = conc. of styrene and benzoyl catalyst resp.; $G$ = constant of the equilibrium; first an additional cpd. is formed between styrene and the catalyst: $Bp + St \rightleftharpoons BpSt$ , this converts into a monomolecular reaction: $BpSt \rightarrow BpSt^*$ or $BpSt \rightarrow Bp + St^*$ ; $St^*$ is the excited styrene molecule which has the ability to polymerize further.	Benzoyl peroxide; the catalyst accelerates polymerization and simultaneously decreases the chain length (polymerization degree); the accelerating action of the peroxide consists not in decreasing the activation heat, but in increasing the action constant by about 5 orders of magnitude; by considering data for the recombination velocities of two radicals the average duration of the growth of a single chain may be estimated; at 100° in 1 mol solution it lies between 10 and 100 sec.	Schultz and Husemann: <i>Z. physik. Chem. (B)</i> , 39, 246-274 (1938).
Polymerization of styrene in $CCl_4$ solution to polystyrene (mol. wt., about 2,000); it is believed that styrene forms with $SnCl_4$ a complex containing HCl added at the double bond; simultaneous introduction of dry HCl forms $\alpha$ -phenyl ethyl chloride, distyrene and low molecular weight polystyrenes $(C_8H_8)_n$ ( $n$ , not greater than 3-4); the amount of distyrene formed depends on the initial amount of styrene; the ratio of $\alpha$ -phenylethyl chloride to distyrene increases greatly with an increase in the initial conc. of styrene and decreases with a decrease in the conc. of the catalyst; the inhibition of polymerization of styrene to form long chains is ascribed to the reaction between styrene molecules (which otherwise would start the polymerization chain) and HCl; velocity of the formation of initial chains estimated to be $7-40 \cdot 10^{16}$ mol/cm <sup>3</sup> sec.; experiments with CP $SnCl_4$ show that inhibition of polymerization by commercial $SnCl_4$ is brought about by traces of HCl present in $SnCl_4$ as an impurity; duration of inhibition up to 4 hrs.; when inhibition is overcome, introduction of moist air for a few minutes causes slowing down of polymerization for an hour; when reaction begins again, air passed through conc. HCl is introduced for a few minutes; then the reaction is discontinued for 2 hrs.	$SnCl_4$ (by using the purest commercial $SnCl_4$ a complete inhibition of the reaction is produced instead of the normal induction period).	Williams: <i>J. Chem. Soc.</i> , 1938, 1046-1052. Williams: <i>Monatsh.</i> , 72, 58-62 (1938).
Polymerization of styrene and methylmethacrylate; T. 80-130°; activation energy, 30.5 K cal.; under identical conditions of temp. and catalysis, the velocity of the reaction is 3 or 4 times greater for pure acrylate than for styrene; the velocity of the mixtures drops rapidly from the value of acrylate to that of styrene when the conc. of the latter increases; thereby it is proved that the measure of chain growth is determinative because the less polymerizable substance, after its entrance into the chain, hinders further growth, so that small additions of this substance strongly decrease the velocity.	Benzoyl peroxide or methylmethacrylate ozonide (obtained by leading ozone into the ester solution); on the basis of Staudinger's theory it is proposed as a reaction scheme that the catalyst decomposing in free radicals produces in a fast reaction with monomers active complexes which, by a reaction with other monomers, form slowly growing chains with a free valence at the end; from time to time the chain is broken off at the cost of a monomer by hydrogenation; thus an active radical is formed, capable of further growth; the number of active germs remains constant and proportional to the conc. of the catalyst; thus the reaction is of a zero order.	Norrish and Brookman: <i>Proc. Roy. Soc. London (A)</i> , 171, 147-71 (1939).

Table 14. Catalytic Polymerization of Ketenes.

Reaction	Catalyst	Observer
Polymerization and auto-oxidation of ketenes; a molecule of unsaturated hydrocarbons reacts with unsymmetrical $O_3$ with an $O_2$ molecule added to the free C valence and an additional hydrocarbon to the $O_2$ valence; formation of a high molecular peroxide results; with an insufficient amount of $O_3$ the chain elongation proceeds with the cumulation of hydrocarbon molecules only; the weak catalytic action of the polymer peroxides may be based on their conversion into monoxides, whereby the O atom set free introduces polymerization.		Staudinger and Lautenschlager: <i>Ann.</i> , <b>488</b> , 1-8 (1931).
Polymerization of ketene ( $CH_2:CO$ ), an anhydride of acetic acid; gaseous ketene does not polymerize at ordinary temp.; impure liquid ketene polymerizes at $80^\circ$ ; pure ketene, stable at $-80^\circ$ ; at $0^\circ$ and in $1\frac{1}{2}$ hrs. completely polymerized to cyclobutadiene; velocities vary, depending upon the DE solvents with high DP which favor polymerization; this reaction not retarded by oxidation agts. such as hydroquinone, by slowing-down agts. nor accelerated by peroxides, such as 1,3-ascaridol or acetone peroxide.		Rice and Greenberg: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 2132-2134 (1934).
Polymerization of ketene; T. 0-100°; pressure, 2-200 atm. product suitable for making films.	Metals: Fe, Ni, Cu.	Wievevich and Gleason: U.S.P. 1,998,404, April 16, 1935.

Table 15. Catalytic Polymerization of Terpenes.

Reaction	Catalyst	Observer
Polymerization of terpene hydrocarbons, such as pinene, at room temp. (conversion, violent); reaction even at $-20^\circ$ possible.	Floridin.	Gurwitsch: <i>Z. physik. Chem.</i> , <b>107</b> , 235 (1923). Venable: <i>J. Am. Chem. Soc.</i> , <b>45</b> , 728 (1923).
Polymerization of terpenes: pinene, dipentene, cedar wood oil in benzene, toluene, xylene or hexane below $15^\circ$ ; only 3/4 of terpenes polymerize, the remainder being unchanged; aromatic hydrocarbons serve as solvents and are quantitatively recovered; no reaction between terpenes and aromatic hydrocarbons takes place.	$AlCl_3$ .	Carmody, M. O. and Carmody, W. H.: <i>J. Am. Chem. Soc.</i> , <b>59</b> , 1312 (1937).
Polymerization of terpenes to diterpenes; mono- or bicyclic terpene hydrocarbons of the composition $C_{10}H_{16}$ to diterpenes of the composition $C_{20}H_{32}$ ; dipentene, $\alpha$ - and $\beta$ -pinene are suitable as initial material.	$H_3PO_4$ or $P_2O_5$ on active charcoal.	I. G. Farbenindustrie A.-G.: F.P. 827,091, April 15, 1938.
Polymerization of diterpene (obtained in previous patent) to cyclic hydrocarbons of the composition $C_{20}H_{32}$ ; T. 200-350°.	Charcoal, infusorial earth, silica gel, glass wool activated by $AlCl_3$ , $ZnCl_2$ , $SnCl_4$ .	I. G. Farbenindustrie A.-G.: F.P. 827,090, April 15, 1938.

Table 16. Catalytic Polymerization of Various Organic Compounds.

Reaction	Catalyst	Observer
Polymerization of turpentine oil (160 parts).	$BF_3$ (1 part).	Berthelot: <i>Ann. chim. phys.</i> (3), <b>38</b> , 41 (1853).
Polymerization of acetaldehyde to paraldehyde (industrial process).	$HCl$ , $SO_2$ , $(COOH)_2$ , $ZnSO_4$ .	Turbaba: <i>Z. physik. Chem.</i> , <b>38</b> , 505 (1901).
Polymerization of hydrocarbons from peat, tar and terpene material to a rubber having strength, stability and vulcanization properties.	Enzymes.	Gottschalk: (1907). Blum: E.P. 28,450 (1908). Callander: E.P. 6,486 (1900). Grist: E.P. 28,613 (1909). Wallace and Morton: E.P. 15,299 (1904). E.P. 27,398 (1909).
Polymerization catalysis.	Oxygen.	Moureu and Dufraisse: <i>Bull. soc. chim.</i> , <b>31</b> , 1152 (1922).

Table 16 (Continued).

Reaction	Catalyst	Observer
Polymerization catalysis.		Carothers, Williams, Collins and Kirby: <i>J. Am. Chem. Soc.</i> , <b>53</b> , 4203 (1931).
Polymerization catalysis.		Milas: <i>Chem. Rev.</i> , <b>10</b> , 324 (1932).
Polymerization catalysis.		Storch: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 374 (1934).
Polymerization catalysis.		Conant and Tongberg: <i>Ibid.</i> , <b>52</b> , 1659 (1930).
Polymerization catalysis.		Conant and Peterson: <i>Ibid.</i> , <b>53</b> , 1058 (1931); <b>55</b> , 1609 (1933).
Polymerization catalysis at high temp. and pressures.	Alumina + Fe.	Ipatieff and Klujkvin: <i>Proc. Roy. Soc. London (A)</i> , <b>186</b> (1924).
Polymerization catalysis.		Ipatieff and Klujkvin: <i>Ber.</i> , <b>58</b> , 4 (1925).
Polymerization of chloral.	Various.	Moureu, Dufraisse and Berchet: <i>Bull. soc. chim. (4)</i> , <b>43</b> , 957-962 (1928).
Polymerization and depolymerization in the treatment of coal; hydrocarbons (acids in aqueous solutions).	Chlorides, peroxides and alkalis of Zn, Al, Sn <sup>IV</sup> and Sb; alkali sulfides and S; phenols, amines, aromatic hydrocarbons act as depolymerizers.	Taylor: <i>Proc. Intern. Conf. Bituminous Coal</i> , <b>1</b> , 190-199 (1928).
Polymerization of indene to polyindenes (hemi-colloidal).	SnCl <sub>4</sub> greater than titanous chloride greater than BCl <sub>3</sub> greater than SbCl <sub>3</sub> and SbCl <sub>5</sub> .	Staudinger, Ashdown, Brunner, Bruson and Wehrli; Gortner, Schiemann and Wiedersheim: <i>Helv. Chim. Acta</i> , <b>21</b> , 934, 958, 962 (1929).
Polymerization of oil.	Addition of S <sub>2</sub> Cl <sub>2</sub> , wood charcoal, dimethyl aniline, little influence; metal oxides: Mn, Pb, Co, greatest influence on the increase in the drying ability of blown oil.	Tschelintzew: <i>Masloboino Zhirovoe Delo (U.S.S.R.)</i> , <b>5</b> , 49-52 (1929).
Polymerization of high molecular weight substances obtained from aliphatic polyhydric alcohols or their derivatives in the presence of O <sub>2</sub> under pressure to non-explosive lubricants; suitable products may be prepared by heating glycerol with caustic alkali or a polymerization catalyst up to 250°; products obtained may be mixed with hygroscopic substances, such as MgCl <sub>2</sub> solution, to impart the desired viscosity; to other lubricants, talc may be added.	HgCl <sub>2</sub> or CuCl <sub>2</sub> .	Noak Lubricants: G.P. 561,199, Aug. 2, 1931.
Polymerization of CO and H <sub>2</sub> to C <sub>6</sub> H <sub>6</sub> at ordinary pressure.	Uranium exceeds thorium as a catalyst.	Fujimura: <i>J. Soc. Chem. Ind. Japan</i> , <b>35</b> , 179B-182B (1932).
Polymerization of mixtures of strong acids and aliphatic cpds.	In case of excess acid, polymerization inhibited by Ni salts.	N. V. de Bataafsche Petroleum Mij: Dutch P. 31,611 (1933).
Polymerization of diphenyl oxide to 75% lubricating oils, 20% tarry substances and 5% gaseous products at 400-800° under pressure.	Al <sub>2</sub> O <sub>3</sub> + CuO.	Dow Chemical Co. (Grebe and Stoesser): U.S.P. 1,905,850 (1934).
Polymerization of methacrylonitrile (as an emulsion, or in the presence of a selective solvent for the monomer).	Benzoyl-acetyl peroxide, H <sub>2</sub> O <sub>2</sub> , O <sub>2</sub> .	Scorah and Wilson: E.P. 419,357, Nov. 2, 1934.
Polymerization of C <sub>6</sub> H <sub>6</sub> (b.p. below 166°); increasing the content of aromatic hydrocarbons from 33% to 44% by volume.	Pt or Al <sub>2</sub> O <sub>3</sub> precipitated on active charcoal.	Zelinsky and Jurjew: <i>Doklady Akad. Nauk. S.S.S.R.</i> , <b>2</b> , 225 (1935).

Table 16 (Continued).

Reaction	Catalyst	Observer
Polymerization in the commercial preparation of polymer $C_6H_6$ ; T. 500°; pressure, 7-13 atm.; yield, 40-80 l. from about 100 cc. initial gas.	$H_3PO_4$ on active substances.	Ipatieff and Egloff: <i>Oil and Gas J.</i> , 33 (52), 31 (1935). Ipatieff and Egloff: <i>Ind. Eng. Chem.</i> , 27, 1067 (1935).
Polymerization of cracking or other olefin-containing gases (to the olefin-containing gas is added 1-6% by volume water vapor with respect to the volume of the cracking gas).	$H_3PO_4$ precipitated on active kieselguhr, charcoal or silica gel.	Universal Oil Products Company (Ipatieff): U.S.P. 2,018,065 (1935). U.S.P. 2,018,066 (1935). Belg. P. 410,799, Sept. 30, 1935.
Polymerization of cyclohexene to tetracyclohexyl benzene and tetracyclohexyl cyclohexene; T. 50-70°.	$AlCl_3$ .	Nametkin and Rudenko: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , 7 (69), 763-775 (1937).
Polymerization of butanes from natural gas (Shamrock Oil and Gas Corp.); butane is cracked and catalytically polymerized, and two products are obtained: (1) by pyrolysis (in butane cracking oven) a polymerization product is formed which is about 8-10% of the total polymer production and partly an absorption oil, which is used again by separation of $CH_4$ ; (2) the catalytic polymerization product which was formed from olefins in the towers containing the catalyst; these products are suitable for mixing with special motor propellants, have a high octane number, a low S and resin content, and are highly sensitive to inhibitors.		Mack: <i>Oil and Gas J.</i> , 37 (No. 51), 60, 62, 64 (1939).
Polymerization of gaseous paraffinic hydrocarbons up to butane containing considerable amounts of propylene and butylene; T. 65-232°; pressure, 7-42 atm.; remaining gas cracked at 48-843° and polymerized at 315-595° under 42-280 atm. pressure using bauxite; hydrocarbons separated have c.p. of benzene, and consist of polymer naphthenes which are hydrogenated to aromatics and gases containing $H_2$ mixed with residue gases of the reaction, and serving the catalytic pressure hydrogenation of unsaturated liquid hydrocarbons obtained in the first stage; residue gas heated at 700-1200° over Si or other substances decreases C precipitation; yield, 75-80% octane, hot polymerization of the same amount of initial products at 75-100° gives a double amount of octane; temp. of adsorption increased; $n$ -butylene, adsorbed; second advantage of the hot process is that the polymer product after formation is taken up by the hydrocarbon phase, and is thus diluted by inert butane; also its activity is decreased and chances for trimer formation, as well as re-arrangement into polymers with low octane number, are less; yield, 85-90% octane; redistillation and mild hydrogenation gives a product of 98-99 octane number.	$H_2SO_4$ on kieselguhr.	Standard Oil Development Co.: F.P. 810,209, March 18, 1937.
	$H_2SO_4$ (63-72% by wt.) the greater the acid phase the faster the reaction; ratio of acid to hydrocarbon, 1': 1 and 2 : 1.	
Polymerization of isobutane (I) and $n$ -butane (II); antiknock benzene is prepared by decomposing the mixture into one fraction rich in isobutane and one fraction rich in $n$ -butane; the isobutane fraction is converted by dehydrogenation at 540° under one atm. in isobutylene (III) and the latter is polymerized at 65-150° and 93-105° to isooctylene; the $n$ -butane is polymerized at 430-650° under more than 35 atm. without a catalyst to benzene; the I fraction, after dehydrogenation, may be polymerized also with a mixture containing olefins (cracking gases) besides I and II so that olefins of the thermal polymerization of the II fraction are not subjected together to it; the method gives better yields, and benzene with better octane number, than polymerization without decomposition in I and II; the isooctylene may be hydrogenated to isooctane; the $H_2$ is gained from the dehydrogenation outlet gases from which ethylene and propylene previously are removed by adsorption in $H_2SO_4$ or by catalytic polymerization.	60-75% $H_2SO_4$ .	Standard Oil Development Co.: F.P. 833,081, Oct. 11, 1938.

Table 16 (Continued).

Reaction	Catalyst	Observer
Polymerization of hydrocarbons to high antiknock cpds., <i>e.g.</i> , a gaseous mixture of butanes and butylenes at normal temp. as contained in cracking gases is liquefied under pressure, purified with NaOH, and led at 115–215° and pressures between 33–51 atm. through a catalyst, whereby the polymerization of butylenes to isooctylenes takes place; the reaction product is then separated from butanes and the butane-free polymerization products are fractionated, whereby the hydrocarbons boiling higher than the octylenes are separated as residue; then the octylenes are subjected to a catalytic hydrogenation in two stages, whereby isooctane is formed.	Ni carbonate precipitated on kieselguhr and then reduced with H <sub>2</sub> ; oxides of Cr, Mo, W are also suitable; a mixture of ortho- or pyrophosphoric acid and kieselguhr.	Universal Oil Products Co.: F.P. 834,170, Nov. 15, 1938.
Preparation of mixed polymers; readily polymerizable cpds. such as vinyl chloride acrylic acid, their ester, metacrylic acid, vinyl ketone, styrene, or isobutylene are polymerized together with difficultly polymerizable organic monocarbonic acids containing olefinic bonds, such as crotonic acid, isocrotonic acid, $\beta$ -methyl crotonic acid, angelica acid, tiglinic acid, $\beta$ -chlorocrotonic acid, cinnamyllic acid, or their esters and nitriles in the presence of catalyst, whereby, the mol ratio of light and heavy polymerizable cpds. is at least 2 : 1, <i>e.g.</i> , 70 parts vinyl methyl ketone (1) together with 44 parts crotonic acid (2) to obtain a solid polymerizate, which is neutralized and is soluble in water; likewise 70 parts (1) together with 37 parts cinnamyllic acid or 80 parts methacrylic acid methyl ester with 20 parts crotonic acid methyl ester.	O <sub>2</sub> -emitting catalysts.	I. G. Farbenindustrie A.-G.: E.P. 499,025, Feb. 16, 1939; Add to E.P. 495,337.
Polymerization of wood tar; T. 250° under atm. pressure; this process is followed by vacuum distillation whereby 30% of a 425° boiling fraction (before treatment 55.3%) and 48% of a fraction boiling between 425° and 572° (before treatment 31.7%) are obtained; the residue is composed of pitch; this treatment prevents the motor fuels from break-down.	ZnCl <sub>2</sub> (5% by weight) or water-free AlCl <sub>3</sub> .	Universal Oil Products Co. (Morrell): U.S.P. 2,123,540, July 12, 1938.
Polymerization of acrylates to water-soluble polymers, <i>e.g.</i> , monomer alkali or NH <sub>4</sub> acrylate or salts of the $\alpha$ -homologs of acrylic acid in the presence of catalysts are heated to about 30°; for acidifying, free acrylic acid or weak organic acids serve, <i>e.g.</i> , propionic acid or butyric acid.	O <sub>2</sub> -emitting, polymerizing catalysts, such as persulfates in weakly acid solution, pH = 4.5–5.5.	I. G. Farbenindustrie A.-G.: E.P. 500,475, March 9, 1939.
Polymerization of acrylic acid, its homologs and derivatives; distillation of crude acrylic acid in vacuum in the presence of hydroquinone; 77% of acrylic acid is obtained with 0.8% SbCl <sub>3</sub> ; under ordinary conditions 88% of acrylic acid is obtained.	0.1–1% anhydrous SbCl <sub>3</sub> , SbCl <sub>5</sub> , AsCl <sub>3</sub> , AsCl <sub>5</sub> , AlCl <sub>3</sub> , or potassium-bismuth iodide.	Imperial Chemical Industries, Ltd. (Crawford): U.S.P. 2,143,941, Jan. 17, 1939.
Polymerization of cracking tar to a black resin of an aromatic nature soluble in benzene; 20% yield; this resin may be used for black lacquers or for the preparation of lampblack; after polymerization the aromatics present in the distillate may be separated more readily than before the polymerization, so that by distillation the following products are obtained: 10% naphthalene, 8% methyl naphthalene, 8% dimethyl	Catalysts used for the Friedel-Crafts reaction.	Monsanto Chemical Co. (Thomas and Taylor): U.S.P. 2,150,641, March 14, 1939.



Table 16 (Continued).

Reaction	Catalyst	Observer
naphthalene, and 27% higher homologs and high-boiling aliphatic hydrocarbons.		
Polymerization of benzene pretreated by Gray's method; the mixture of a polymerization benzene and straight-run benzene possesses a susceptibility equal to that of ordinary cracking benzene.	Small amounts of ordinarily used inhibitors cause the same favorable action as in the case of cracking benzene.	Ross and Henderson: <i>Refiner Natural Gasoline Mfr.</i> , <b>18</b> , 140-43. Ross and Henderson: <i>Oil and Gas J.</i> , <b>37</b> (Nr. 45), 107-08 (1939).
Polymerization of fatty oils which are added to lubricating oils and increase their viscosity; prepared from semi-drying oils, such as rape, cottonseed, and fish oils in a mixture with palm oil or grease by heating to 260-270° in a special apparatus under diminished pressure; likewise polymerization is carried out with 10-60% of a cylinder oil.	Metallic soaps in amounts 0.01-0.02%.	Standard Oil Development Co. (Froelich and Wasson): U.S.P. 2,150,370, March 14, 1939.

Table 17. Catalytic Polymerization and Isomerization.

Reaction	Catalyst	Observer
Polymerization and isomerization of pinene to 20% dipinene.	Japanese acid earth.	Kuwata: <i>J. Soc. Chem. Ind. Japan</i> , <b>32</b> , 372B (1929).
Polymerization and isomerization of pinene.	Si substituted; waste products obtained by treatment of Al salts from clays by acids.	Daschnewitsch and Wolnow: Russ. P. 48,306, Aug. 31, 1936.
Review of polymerization of unsaturated cpds.		Burk: <i>Ind. Eng. Chem.</i> , <b>30</b> , 1054-1063 (1938).
Polymerization and isomerization in the case of highly unsaturated hydrocarbons and their derivatives.		Paworski: <i>Izvest. Akad. Nauk. S.S.S.R.</i> , 1937, 979-1000.
Polymerization (mechanism).		Husemann: <i>Rundschau deut. Tech.</i> , <b>18</b> (38), 8-9 (1938).

## PART XVIII

## Catalytic Isomerization in Organic Chemistry

Table 1. Catalytic Isomerization of Paraffinic Hydrocarbons.

Reaction	Catalyst	Observer
Isomerization in the pyrolysis of isopentane with the addition of propane, butane and isobutylene; formation of <i>cis</i> - and <i>trans</i> -2-butene.		Frey and Hepp: <i>Ind. Eng. Chem.</i> , <b>25</b> , 441 (1933).
Isomerization and polymerization of <i>n</i> -heptane: (1) T. 300°; yield 27%. (2) T. 400°; yield 18%. (3) T. 400°; yield 15%.	(1) 5% ZnCl <sub>2</sub> . (2) 1% AlCl <sub>3</sub> . (3) 5% MoS <sub>3</sub> .	Petrow, Meschtscherjakow and Andrejew: <i>Ber.</i> <b>68</b> , 1 (1935).
Isomerization of <i>n</i> -hexane; T. 20-90°C.; yield, 2-28%.	AlCl <sub>3</sub> and propyl chloride.	Moldavskii, Kobilskaia and Livschitz: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>5</b> (67), 1791 (1935).
Isomerization of <i>n</i> -butane to isobutane; T. 27°; yield, 18-22 mol % <i>n</i> -butane and 78-82 mol % isobutane; equilibrium mixture attained after 2 months.	5 mol % AlBr <sub>3</sub> .	Montgomery, McAteer and Franke: <i>J. Am. Chem. Soc.</i> , <b>59</b> , 1768-1769 (1937).
Isomerization of <i>n</i> -octane in a stream of H <sub>2</sub> ; T. 300-310°; yield: (1) 15.0%. (2) 5.5%. (3) 10.0%.	(1) Pt on active charcoal. (2) Ni (23%) on Al <sub>2</sub> O <sub>3</sub> . (3) Ni (21%) on ZnO.	Jurjew and Pawlow: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> <b>7</b> (69), 97-99 (1937).

Table 1 (Continued).

Reaction	Catalyst	Observer
Isomerization of paraffinic hydrocarbons (from straight-chain hydrocarbons to branched chain hydrocarbons):	Halides of Al, Zn, Sn, Fe, Zr, Be, Nb, Ta, B and a small amount of H <sub>2</sub> halide.	Universal Oil Products Company; F.P. 823,595, Jan. 22, 1938.
n-butane (100 parts) to isobutane; T. 150°; pressure, 30 atm.; time, 12 hrs.; yield, 66.5%;	AlCl <sub>3</sub> (20 parts) and HCl (2 parts).	
n-pentane to isopentane; T. 200°; pressure, 30 atm. in a streaming system; yield, 27%.	AlCl <sub>3</sub> on active charcoal in the presence of HCl.	

Table 2. Catalytic Isomerization of Cyclic Hydrocarbons.

Reaction	Catalyst	Observer
Isomerization of cyclohexane to methylcyclopentane.	AlCl <sub>3</sub> .	Aschan: <i>Ann.</i> , <b>324</b> , 1 (1902). Grignard and Stratford: <i>Compt. rend.</i> , <b>178</b> , 2149 (1924).
Isomerization of cyclohexane to methylcyclopentane at 500° under high pressure.	Al <sub>2</sub> O <sub>3</sub> .	Ipatieff and Dowgalewitsch: <i>Ber.</i> , <b>44</b> , 2987 (1911). Ipatieff and Huhn: <i>Ber.</i> , <b>36</b> , 2014 (1903).
Isomerization of cyclohexane to methylcyclopentane and dimethylcyclobutane.	AlCl <sub>3</sub> (anhydrous). AlBr <sub>3</sub> .	Zelinsky and Turowa-Pollak: <i>Zhur. Priklad. Khim. (U.S.S.R.)</i> , <b>7</b> , 753-756 (1934). Zelinsky and Turowa-Pollak: <i>Ber.</i> , <b>65</b> , 1171 (1932).
Isomerization of cyclohexane to methylcyclopentane; yield, 22.8%.	H <sub>2</sub> O, promoter. AlCl <sub>3</sub> , catalyst.	Nenitzescu and Cantuniari: <i>Ber.</i> , <b>66</b> , 1097 (1933).
Isomerization of cyclohexane derivatives: methyl, dimethyl and ethyl to 5-member ring cpds.; T. 120-130°C.	10% AlCl <sub>3</sub> (anhydrous).	Turowa-Pollak and Zelinsky: <i>Ber.</i> , <b>68B</b> , 1781 (1935).
Isomerization of cyclopropane:		Ipatieff and Huhn: <i>Ber.</i> , <b>36</b> , 2014 (1903).
$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_3\text{CH} \quad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$		
$\begin{array}{l} \nearrow \text{CH}_2\text{CH}=\text{CHCH}_3 \\ \searrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \end{array}$	β-butylene.  α-butylene.	
Isomerization of cyclopropane to propene; T. 400-405°C. T. 500°C. only 20 min. necessary for the reaction.		Engler: "Die Entstehung des Erdöls," Fortschritte der Naturwiss. Forschung (Berlin) pp. 269-306 (1910). Routala: Dissertation, p. 49, Karlsruhe, 1909.
Isomerization of methylenecyclobutane to methylcyclobutene; T. 300°.	Al <sub>2</sub> O <sub>3</sub> .	Filipov: <i>J. prakt. Chem.</i> , <b>93</b> , 162-182 (1916); refer also to Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," p. 159, Macmillan Co., 1936.
$\begin{array}{ccc} \text{CH}_2 & \text{C}=\text{CH}_2 & \text{CH}_2 \text{ C CH}_3 \\   & &   \\ \text{CH}_2 & \text{CH}_2 & \text{CH}_2 \text{ CH} \end{array} \rightarrow$		
Isomerization of methylenecyclobutane to methylenecyclobutene; T. 300°; methylene cyclobutene is converted to isoprene with splitting of the ring; T. 400-430°.	Al <sub>2</sub> O <sub>3</sub> .	Dojarenko: <i>J. Russ. Phys. Chem. Soc.</i> , <b>58</b> , 1-18, 16-26, 27-38 (1925). Dojarenko: <i>Ber.</i> , <b>59</b> , 2933-2948 (1926).
Isomerization of cis-(0,3,3)-bicyclooctane to (1,2,3)-bicyclooctane at room temp.	AlCl <sub>3</sub> .	Barrett and Linstead: (1936).
Isomerization of naphthenes.	AlCl <sub>3</sub> , ZrCl <sub>4</sub> .	Ipatieff and Grosse (U.O.P. Co.).
Isomerization of isopropylether of m-cresol to thymol with 1-methyl-6-isopropyl-3-oxylene; T. 320-350°; pressure increased to 60 atm.; time, several hrs.	Silica gel (10% of the weight of the charge).	Shering-Kahlbaum A.-G. (Schoeller, Jordan and Clerc); G.P. 520,859 (1931).


Table 2 (Continued).

Reaction	Catalyst	Observer
Isomerization of phenylcyclohexylether to <i>p</i> -cyclohexylphenol (the alkyl migrates from O to the ring C).		
Isomerization of oxides of cyclic olefins to cyclic ketones: oxides of 1-menthene, 3-menthene, cyclohexene, methylcyclohexene, camphene (in vapor phase) to the corresponding ketones; 10 parts 3-menthene oxide to ketone; T. 250°; time, 2 hrs.	Silica gel or kieselguhr.  0.5 part silica gel.	Shering-Kahlbaum A.-G. (Schöeller, Schwenk and Borgwardt): G.P. 566,156 (1932).
Isomerization of alkyl cyclopentanes; it is found that alkyl cyclopentane is converted at 50° over the catalyst AlCl <sub>3</sub> in 80% methylcyclohexane; ethylcyclopentane gives methylcyclohexane; propyl- and isopropylcyclopentane gives 1,3-dimethylcyclohexane, while <i>n</i> -, <i>sec</i> -, and <i>tert</i> -butylcyclopentane are converted into 1,3,5-trimethylcyclohexane; the structure of conversion products is determined by dehydrogenation to the corresponding aromatic hydrocarbons with platinized Al <sub>2</sub> O <sub>3</sub> , followed by bromination or nitrogenation; alkyl cyclopentanes are not dehydrogenated under the applied conditions; the conversion proceeds in all probability through polymethylcyclopentane, which then changes into methyl- as well as polymethylcyclohexane.	AlCl <sub>3</sub> .	Pines and Ipatieff: <i>J. Am. Chem. Soc.</i> , <b>61</b> , 1076-77 (1939); refer also to Nenitzescu and Cantunari: (Refer to C. 1933 II 1672).

Table 3. Catalytic Isomerization of Olefinic Hydrocarbons.

Reaction	Catalyst	Observer
Isomerization of 1,1-dimethyltrimethylene and vinyl trimethylene to hydrocarbons, of the allene series; T. 340-345.	Al <sub>2</sub> O <sub>3</sub> .	Ipatieff and Huhn: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>35</b> , 603 (1903). Ipatieff: <i>Ibid.</i> , <b>36</b> , 760 (1904).
Isomerization of trimethylethylene; no free radical formation necessary to explain the mechanism of isomer formation; it is assumed that a proton is added to the double bond which leaves 1 C atom with only 6 electrons, 2 electrons lacking a stable configuration, and this induces a rearrangement of atoms resulting in the formation of isomeric cpds.		Laughlin, Nash and Whitmore: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 1395 (1934).
Isomerization of isopropylethylene to trimethylethylene.	Alumina.	Ipatieff: "Catalytic Reactions at High Pressures and Temperatures," pp. 127, 141, The Macmillan Co., New York, 1936.
$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH}_2 \end{array} \text{CHCH=CH}_2 \rightarrow \begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{CHCH}_3 \\ \diagup \\ \text{CH}_3 \end{array}$		
Isomerization of isopropylethylene to trimethylethylene.	Al <sub>2</sub> O <sub>3</sub> .	Ipatieff: "Aluminum Oxide as a Catalyst in Organic Chemistry," p. 34, Leipzig, 1927.
Isomerization of butylenes at high temp. and pressures; T. 440-450°.	Alumina in a copper tube.	Ipatieff and Sdzitowecy: <i>Ber.</i> , <b>40</b> , 1827 (1907).
Polymerization of styrene to the distyrene structure of 1,3-diphenyl-1-butene (C <sub>6</sub> H <sub>5</sub> CH=CH-CHCH <sub>3</sub> ) C <sub>6</sub> H <sub>5</sub> which isomerizes to 1,3-diphenyl-2-butene.	HCl, or 1 part H <sub>2</sub> SO <sub>4</sub> · 9 parts glacial acetic acid.	Stoppe, and Posnjak: <i>Ann.</i> , <b>371</b> , 287 (1910).
Isomerization of phenylated butene dimer to saturated cyclobutane dimer with benzophenone as the oxidation product; T. 215°; time, 6 hrs.	Floridin.	Lebedew, Andrewsky and Mantushkina: <i>Ber.</i> , <b>56</b> , 2349 (1923).
Isomerization of butylene.	Alumina.	Matignon, Moureau and Dode: <i>Compt. rend.</i> , <b>196</b> , 1560-1563 (1933).

Table 3 (Continued).

Reaction	Catalyst	Observer
Isomerization of 1-butene to 2-butene; T. 400°.	Silica gel or bauxite.	I. G. Farbenindustrie A.-G. (Runge and Müller-Cunradi): G.P. 583,790 (1933).
Isomerization of normal butenes: (1) 1-butene to 2-butene; complete isomerization at 249° and 7.8 atm. pressure; yield, small, at room temp.; (2) 1-butene to <i>cis</i> -2-butene (6.0%) and <i>trans</i> -2-butene (6.6%) at high temp. and pressures; (3) partial isomerization of 1-butene to 2-butene at various temp. under atmospheric and high pressures and various contact times.	H <sub>2</sub> PO <sub>4</sub> (100%).  Diatomaceous earth impregnated with H <sub>2</sub> PO <sub>4</sub> .  HClO <sub>4</sub> and aqueous solutions of ZnOCl and C <sub>6</sub> H <sub>5</sub> ·SO <sub>3</sub> H.	Ipatieff, Pines and Schaad: <i>J. Am. Chem. Soc.</i> , <b>56</b> , 2696 (1934).
Isomerization of 1-octene to 2-octene; T. 140–150°C.	Alcoholic potash.	Behal: <i>Bull. soc. chim.</i> , <b>49</b> , 581 (1888). Behal: <i>Ann. chim. phys.</i> (6), <b>15</b> , 408 (1888). Desgraz: <i>Ibid.</i> , (7), <b>3</b> , 209 (1894).
Isomerization of 2-octene to 1-octene; T. 110° C.	Metal Na.	
Isomerization of a mixture containing 80% 1-heptene to 2-heptene; T. 380°C.; yield, 70%; no rearrangement occurred either at 250° or at 350°.	Soda lime in an iron tube.	Guest: <i>J. Am. Chem. Soc.</i> , <b>50</b> , 1744 (1928).
Preparation of isobutane from <i>n</i> -butane; gas mixtures containing <i>n</i> -butane are treated in the liquid phase at room temp., or slightly higher (below 110°), with small amounts of H <sub>2</sub> halides; best to work at 10–30° and under 3 atm. pressure.	AlCl <sub>3</sub> or AlBr <sub>3</sub> .  AlCl <sub>3</sub> and AlBr <sub>3</sub> mixed with pumice or silica gel.	N. V. deBataafsche Petroleum Maatschappij: F.P. 841,979, June 2, 1939. N. V. deBataafsche Petroleum Maatschappij: Belg. P. 429,747 and 429,748, Aug. 17, 1938.
Isomerization of dimethylvinyl-ethylene oxide into 2,2-dimethylbutene-(3)-al; dimethylvinyl-ethylene is obtained by: (1) reduction of mesityloxide with Al isopropylate; (2) distillation of the alcohol formed over H <sub>2</sub> SO <sub>4</sub> on pumice; dimethylvinylethylene oxide: (1) (CH <sub>3</sub> ) <sub>2</sub> C=CH·CH <sub>2</sub> : 		Ives Deux: <i>Compt. rend.</i> , <b>207</b> , 920–21 (1938).
obtained from dimethylvinylethylene by conversion with urea chloride in dilute acetic acid and treatment of the chlorhydrine with solid KOH in ether; finally 2,2-dimethylbutene-(3)-al-(1); (2) CH <sub>3</sub> :CH·C(CH <sub>3</sub> ) <sub>2</sub> :CHO is formed from dimethylvinylethylene oxide by distillation over kieselguhr at 250° or by treatment with MgBr <sub>2</sub> etherate; 2,2-dimethylbutanol-(1) is obtained by hydrogenation of 2,2-dimethylbutene-(3)-al-(1), or from C <sub>2</sub> H <sub>5</sub> ·C(CH <sub>3</sub> ) <sub>2</sub> ·MgCl and ethyl formate.		
Isomerization of dipropenyl glycol to dibutylal; K <sub>p</sub> <sub>17</sub> = 65° D <sub>17</sub> <sup>20</sup> = 0.909 n <sub>D</sub> <sup>20</sup> = 1.408 yield, 50%; T. 130° formation of dibutylal starts at 90°; at 110°, in addition to dibutylal, is obtained an isomeric octene-(2)-ol-(4)-on-(5), C <sub>8</sub> H <sub>16</sub> O <sub>2</sub> ; K <sub>p</sub> <sub>18</sub> = D <sub>18</sub> <sup>20</sup> = 0.9426 n <sub>D</sub> <sup>20</sup> = 1.4485; the Raman spectrum of the intermediate compound permits the conclusion that an isomer with double bond at the end is present.	Cu or Al <sub>2</sub> O <sub>3</sub> .	Martineau and Wiemann: <i>Compt. rend.</i> <b>207</b> , 243–245, 411 (1938); refer also to Urion, Thesis, Paris, 1933.

Intermediate Compound

CH<sub>3</sub>:CH:CH·CH(OH)·CO·C<sub>2</sub>H<sub>5</sub>

Table 4. Catalytic Isomerization of Olefinic Oxides.

Reaction	Catalyst	Observer
Isomerization in the metameric rearrangement of alkylene oxides: trimethylethylene oxide to methylisopropyl ketone or aldehyde; T. 200–300°.	Al <sub>2</sub> O <sub>3</sub> .	Ipatieff and Leontowitsch: <i>J. Russ. Phys.-Chem. Soc.</i> , <b>35</b> , 606 (1903).
Isomerization of alkylene oxides to aldehydes: (1) ethylene oxide to acetaldehyde; (2) propylene oxide to propyl aldehyde; (3) isobutylene oxide to isobutyl oxide; (4) methylethylene oxide to methylethyl acetaldehyde.	Cpds. of the 5th and 6th groups of the Periodic System such as Mg pyrophosphate precipitated on kieselguhr.	I. G. Farbenindustrie A.-G.: E.P. 331,185 (1930).
Isomerization of ethylene oxide to acetaldehyde; T. 220°; velocity of passage, 120–200 g./hr./l. contact space; yield, 75% acetaldehyde and 25% unchanged ethylene oxide as well as higher-boiling products.	Fine silica gel dust mixed with water to a stiff paste, evaporated to dryness on a water bath, broken into pieces and dried in vacuum.	Rheinische Kampfer Fabrik A.-G. (Rathol): G.P. 547,641 (1931).
Isomerization of (1) propylene oxide in vapor phase to propionaldehyde (60%) and acetone (20–25%); T. 330–350°; time, 1 hr. at 100 g./l. catalyst; (2) equal volumes of propylene oxide vapor and N <sub>2</sub> led over the catalyst at 300°; yield, propionaldehyde (60%) and acetone (15%).	(1) BaBr <sub>2</sub> heated in a stream of air at 350°, ground in a round mill, and mixed intimately with one-half its weight kieselguhr; (2) MgOCl, Mg phosphate and bleaching earth in equal parts ground together and dried in a stream of air at 350°.	I. G. Farbenindustrie A.-G. (Bauer): G.P. 535,651 (1931).
Isomerization of propylene oxide to propionaldehyde; T. 250–400°; propionaldehyde is heated in a second contact chamber in the presence of H <sub>2</sub> to propyl alcohol; T. 125–170°.	Al <sub>2</sub> O <sub>3</sub> . Ni.	Carbide & Carbon Chemicals Corp. (Young and Law): U.S.P. 1,953,548 (1934).
Isomerization of propylene oxide vapor to propionaldehyde; T. 300°; yield, 70% of the theoretical.	Silica gel (3–6 mm. size of pieces); natural or activated Al silicate.	I. G. Farbenindustrie A.-G. (Hoffmann): G.P. 618,972 (1935).
<i>Cis-trans</i> isomerization of pure isostilbene in benzene in darkness for two hours (independent of the presence of air, vacuum, or antioxidants); the conversion velocity depends on the amount of peroxide; the <i>cis-trans</i> isomerization of isostilbene in benzene solution in light takes place in 5 min.; evacuating the reaction container causes the reaction to proceed completely in 20 min. and this time antioxidants prevent the reaction completely; also prevented in the presence of air; with HCl, no isomerization is observed under any conditions; this is explained by the relative oxidation stability of this cpd.; in darkness, no conversion with HBr + Br <sub>2</sub> mixture; the mechanism of the reaction once induced is considered that of a chain.	HBr; bromine atoms are considered to be active catalysts of isomerization.  HBr–Br <sub>2</sub> .	Kharash, Mansfield and Mayo: <i>J. Am. Chem. Soc.</i> , <b>59</b> , 1155 (1937).
Isomerization of isostilbene to stilbene.	O <sub>2</sub> similar to peroxide strongly accelerates isomerization; reduced Ni produces in general catalytic action analogous to that of O <sub>2</sub> ; also influences isomerization of isostilbene, but in a weaker manner; Kharash's opposite findings are due to the presence of too small amounts of O <sub>2</sub> ; isostilbene does not form a peroxide with O <sub>2</sub> in darkness or in diffuse light; it is assumed that the effect of molecular oxygen is involved.	Urushibara and Simamura: <i>Bull. Chem. Soc. Japan</i> , <b>12</b> , 507–509 (1937); refer also to Kharash, Mansfield and Mayo: (Refer to C. 1938 II 3227.)

Table 5. Catalytic Isomerization of Diolefins.

Reaction	Catalyst	Observer
Isomerization of diolefins to divinyl derivatives: diallyl as well as di-isobutenyl; T. 325°.	Floridin.	Lebedew and Slobodin: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>4</b> , 23, (1934).
Isomerization of diallyl to dipropenyl (double bond shifted) in the presence of CO <sub>2</sub> ; two stages: (1) T. 200°. (2) T. 300°.	(1) 30% Pt asbestos. (2) 30% Pt charcoal.	Lewina: <i>Ibid.</i> , <b>6</b> , 1092 (1936).
Isomerization of 2,4-dimethylpentadiene-1,3-tetramethylallene (a cpd. with a conjugated double bond is changed to one with a simple double bond).	Floridin.	Slobodin: <i>Ibid.</i> , <b>6</b> , 1806 (1936).
Isomerization of halogen butadiene, e.g., 100 g. chlor-4-butadiene-1,2 added to 300 cc. 18.5% aqueous hydrocarbons containing 20 g. CuCl <sub>2</sub> to 75 g. pure chlor-2-butadiene-1,3; T. 26°; stirred for 4 hrs. and then distilled with vapor; chlor-4-butadiene-1,2 + NaI in 80% alcohol gives iodine-4-butadiene-1,2; with diluted HCl and CuCl <sub>2</sub> , iodine-2-butadiene-1,3 is formed.	Organic bases, acids, metals, HCl, CuO in water, FeCl <sub>3</sub> (anhydrous), C <sub>2</sub> H <sub>5</sub> OH + CuCl <sub>2</sub> or AuCl <sub>3</sub> + HCl.	Dupont (Carothers): U.S.P. 2,104,789, Jan. 11, 1938.

Table 6. Catalytic Isomerization of Acetylene.

Reaction	Catalyst	Observer
Isomerization of propyl acetylene to methylethyl acetylene; T. 170°; time, 24 hrs.	Alcoholic potash, or alcoholic soda, or Na alcoholate.	Faworsky: <i>J. prakt. Chem.</i> (2), <b>37</b> , 384 (1888).
Isomerization of isopropyl acetylene to isoprene; T. 400°; pressure, 50 mm. (CH <sub>3</sub> ) <sub>2</sub> CH · C · CH = CH <sub>2</sub> :C · CH(CH <sub>3</sub> ):CH <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Ipatieff: "Aluminum Oxide as a Catalyst in Organic Chemistry," p. 36, Leipzig, 1929.

Table 7. Catalytic Isomerization of Allene.

Reaction	Catalyst	Observer
Isomerization of asymmetrical dimethyl allene to isoprene under diminished pressure.	Al <sub>2</sub> O <sub>3</sub> .	Ipatieff: <i>Ibid.</i> , p. 35.
Isomerization of asymmetrical dimethyl allene to isoprene and isopropyl acetylene; T. 215°; at 280° yield of isoprene increases up to 20%; at 334° yield of isopropyl acetylene increases up to 60%.	Floridin activated at 325°.	Slobodin: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>4</b> , 778 (1934).
Isomerization of methyl allene to 3.4% ethyl acetylene and traces of divinyl; T. 245–330°C.	Floridin.	Slobodin: <i>Ibid.</i> , <b>5</b> , 48–52 (1935).
Isomerization of allene to allylene at high temp.	Floridin.	Slobodin: <i>Ibid.</i> , <b>6</b> , 1892 (1936).
Isomerization of 1-alkene to allene instead of 2-alkene.	Na alcoholate.	Hurd: Private Communication (1935).
Isomerization of allene hydrocarbons:		Slobodin: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>7</b> (69), 2376–2380 (1937).
(1) methyl allene to ethyl acetylene and divinyl; in the absence of double-substituted acetylene, the dimethyl acetylene;	Floridin.	Slobodin: (Refer to C. 1936 II 3089).
(2) ethyl acetylene (also dimethyl acetylene) to methyl allene (identified as liquid tetrabromide), divinyl and dimethyl acetylene (small amount); T. 275°;	Floridin.	<i>Zhur. Obshchei Khim. (A)</i> , <b>5</b> (67), 48–52 (1935).
(3) dimethyl acetylene to ethyl acetylene (5–14%), methyl allene (smaller amount than in previous cases); divinyl, absent; three times through at 278–285° gave only 36.7%.	Floridin.	

Table 7 (Continued).

Reaction	Catalyst	Observer
Isomerization of allene hydrocarbons, e.g., 1-phenylbutene-3 isomerizes with difficulty over floridin activated in usual manner at 250°; the following reaction course is postulated:	Silicate catalyst.	Slobodin: <i>Zhur. Obshchei Khim.</i> , 9, 272-276 (1939).
$  \begin{array}{ccccccc}  \text{C}_6\text{H}_5 & \text{C}_6\text{H}_5 & \text{C}_6\text{H}_5 & \text{C}_6\text{H}_5 & \text{C}_6\text{H}_5 & \text{C}_6\text{H}_5 & \text{C}_6\text{H}_5 \\    &   &   &   &   &   &   \\  \text{CH}_2 & \text{CH}_2 & \text{CH}_2 & \text{CH}_2 & \text{CH} & \text{CH} & \text{CH} \\    &   &   &   &   &   &   \\  \text{CH}_2 & \rightleftharpoons \text{CH} & + \text{H} \rightleftharpoons \text{CH} & + \text{H} \rightleftharpoons \text{CH} & \rightleftharpoons \text{CH} & + \text{H} \rightleftharpoons \text{CH} & + \text{H} \rightleftharpoons \text{CH} \\    &   &   &   &   &   &   \\  \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} \\     &    &    &    &   &   &   \\  \text{CH} & \text{CH} & \text{CH} & \text{CH} & \text{CH} & \text{CH} & \text{CH} \\  & & & & & &   \\  & & & & & & \text{CH}_2  \end{array}  $		

however, 1-phenylbutadiene-1,3 and methylbenzyl acetylene are not found among the reaction products, while the presence of small amounts of benzyl allene is possible; the butadiene converts very easily under the reaction conditions in a monosubstituted acetylene, while benzyl allene is not stable.

Isomerization of allene hydrocarbons; by splitting off HBr from bromhydrine of cinnamic alcohol at 150-175°, using powdered KOH, a hydrocarbon mixture is formed which does not contain benzyl acetylene, but consists of 63.5% phenyl allene and 36.5% methylphenyl acetylene; these data were calculated from the ratio $\text{HCOOH} : \text{CH}_3\text{COOH}$ of the ingredients of the ozonization product (in chloroform at -45°); according to concepts previously developed by the author the methylene hydrogen atoms of benzyl acetylene are mobile because they stand in the $\beta$ -position to the benzene nucleus and the triple bond, so that the conversion into methylphenyl acetylene may occur readily; a partial conversion of phenyl allene in benzyl acetylene could take place, although such a conversion does not take place directly on the silicate catalyst.	Silicate catalyst.	Slobodin: <i>Ibid.</i> , 8 (70), 1220-1223 (1938).
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Table 8. Catalytic Isomerization of Acids.

Reaction	Catalyst	Observer
Isomerization of oleic acid to alaidic acid.	Nitrous acid.	Fischer: <i>Ber.</i> , 26, 2400 (1893); 27, 615 (1894).
Isomerization of maleic to fumaric acid; this process is not according to the scheme: $\text{COOH} \cdot \text{CH}=\text{CH} \cdot \text{COOH} \rightleftharpoons \text{COOH} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{COOH}$ ; rather the mechanism involves H ions which facilitate the reaction by combining groups connected with the double bond or through the ionic field which causes distortion or expansion of the double bond.	H ions (aqueous solution of HCl highly conc. in D; no D enters the group $-\text{CH}=\text{CH}-$ ).	Horrex: <i>Trans. Far. Soc.</i> , 32, 570-571 (1937).
Thermal isomerization of cinnamic acid to <i>cis</i> - and <i>trans</i> -cinnamic acid; T. 99.4° and 122.5°; the reaction to <i>cis</i> -cinnamic acid is of the first order; the reaction to <i>trans</i> is of the $\frac{1}{2}$ order; from this it is concluded that catalysis takes place by atomic iodine.	Iodine in benzene (catalysis through atomic iodine).	Dickinson and Lotzkar: <i>J. Am. Chem. Soc.</i> , 59, 472-475 (1937).

Table 9. Catalytic Isomerization of Aromatic Hydrocarbons.

Reaction	Catalyst	Observer
Isomerization of pentamethylbenzene to small amount of isodurene; T. 50-55°C.; time, 14 days.	$\text{AlCl}_3$ (half the weight of the substances to be isomerized).	Jacobsen: <i>Ber.</i> , 18, 338 (1885).
Isomerization of pentamethylbenzene to large amount of durene and isodurene; T. 100-110°; time, 4 hours.	HCl.	
Isomerization of allyl benzene to propenyl benzene: T. 500°C.	Infusorial earth.	Ramart-Lucas and Amagat: <i>Compt. rend.</i> , 188, 638 (1929).

Table 9 (Continued).

Reaction	Catalyst	Observer
Isomerization of unsaturated hydrocarbons with a double bond in the $\alpha$ - $\beta$ position:	30% Pt on charcoal.	Lewina and Petrow: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>7</b> (69), 747-749 (1937). (Refer to C. 1929 II 2045.)
(1) <i>p</i> -allyl toluene with CO <sub>2</sub> to 84% <i>p</i> -propenyl toluene and 16% unchanged <i>p</i> -allyl toluene; T. 300°;		Zelinsky and Lewina: <i>Ber.</i> , <b>62</b> , 1861-63 (1929).
(2) allyl benzene to a mixture of unchanged hydrocarbons and $\alpha$ - $\beta$ isomers; it has been proved that the double bond in the side chain of <i>p</i> -allyl toluene and $\gamma$ -butenyl benzene is displaced under the catalytic influence of Pt in the direction of the aromatic nucleus whereby stable isomeric cpds. are formed.		
Isomerization of hexahydro- <i>o</i> -cresol to methylcyclohexane.	Ni <sub>2</sub> O <sub>3</sub> .	Ipatieff: <i>Ber.</i> , <b>36</b> , 2000 (1903).
Isomerization of methylcyclohexanol.	Alumina.	
Isomerization of <i>cis</i> - to <i>trans</i> -Decalin.		Zelinsky and Turowa-Pollak: <i>Ber.</i> , <b>58</b> , 292-298 (1925).
Isomerization of decahydronaphthalene and dehydrogenation of Decalin.		
Isomerization in the displacement of the radical from N to the ring carbon; N-alkylated, N-cycloalkylated, or N-alkylated secondary or tertiary aromatic amines cause the migration of N-bound radical to the C atom in the ring: methylaniline to <i>p</i> -toluidine; T. 350°.	Silicic acid.	Inoue: <i>Bull. Chem. Soc. Japan</i> , <b>1</b> , 157 (1926).
	Japanese acid earth (washed with water).	
Isomerization of 1-phenylindene to $\alpha$ - and $\beta$ -phenylindene.	Pd.	von Braun and Manz: <i>Ber.</i> , <b>62</b> , 1059 (1929).
Isomerization of $\alpha$ - <i>p</i> -tolylindene to $\beta$ -tolylindene; yield, one-half of that obtained for phenylindene.		
Isomerization of thymol isomers (m.p. 69°F. or m.p. 112°F.) to 60% thymol, 15% <i>m</i> -cresol and 5% dipropyl- <i>m</i> -cresol; T. 230°; time, 12 hrs. (heated in an autoclave).	Kieselguhr, silica gel, Al <sub>2</sub> O <sub>3</sub> , natural and active earths, or active charcoal; 10% active bleaching earth.	Rheinische Kampfer Fabrik A.-G.: E.P. 326,215 (1930).
Isomerization of $\alpha$ -methyl naphthalene to $\beta$ -methyl naphthalene in the presence of air or H <sub>2</sub> ; T. 420°.	Silicic acid gel.	Mayer and Schiffner: <i>Ber.</i> , <b>67</b> , 67 (1934).
Isomerization of $\alpha$ -ethyl naphthalene to $\beta$ -ethyl naphthalene in the presence of N passed over the catalyst; T. 420-430°; a rearrangement of the alkyl group or phenyl group in the naphthalene molecule, likewise (with ease) of $\alpha$ -phenyl.	Silicic acid gel.	
Isomerization of 1,6-dimethyl naphthalene to $\beta$ -phenyl naphthalene; T. 420°.		
Isomerization of $\alpha$ - to $\beta$ -phenyl naphthalene; T. 350°.		
Isomerization of $\alpha$ - to $\beta$ -brom naphthalene.		
Isomerization of N-monoethyl- <i>o</i> -toluidine (300 g.) to 2-methyl-4-ethyl aniline (oil); T. 220-230°; time, 12 hrs.; yield, 80%.	40 g. K alum containing active bleaching earth; acid-free ton or kaolin; activated silicates, activated hydrosilicates treated with acids.	I. G. Farbenindustrie A.-G.: E.P. 421,791 (1935). F.P. 776,124 (1934). Rheinische Kampfer Fabrik A.-G. (Schollkopf): E.P. 319,205 (1929). F.P. 681,049 (1930).



Table 9 (Continued).

Reaction	Catalyst	Observer
Isomerization of phenyl ethers to alkylated phenols.	H <sub>3</sub> PO <sub>4</sub> .	Ipatieff and Pines (U.O.P. Co.).
Isomerization of <i>n</i> -brombenzanilide in chlorobenzene; T. 25°; the reaction mechanism is assumed to be the participation of free radicals and the formation of a reaction chain; altogether different results were obtained with <i>n</i> -brom- $\omega$ -chlor- and <i>n</i> -brom- $\omega$ , $\omega$ , $\omega$ -trichlor-acetanilide; it is believed that a chain mechanism is chiefly involved here.	Trichloroacetic acid has a catalytic constant ( $K_A \cdot 10^4 = 1050$ ); dichloroacetic acid = 153; phenylpropionic acid = 60; monochloroacetic acid = 20; <i>m</i> -nitrobenzoic acid = 10.9; $\beta$ -chloropropionic acid = 5.3; phenylacetic acid = 5.6, acetic acid = 3.4; $K_A$ changes slightly with the acid conc., i.e., linearly.	Bell and Lidwell: <i>J. Chem. Soc.</i> , <b>1939</b> , 1096-99.

Table 10. Catalytic Isomerization of Terpenes.

Reaction	Catalyst	Observer
Isomerization of pinene.		Zelinsky: <i>Ber.</i> , <b>58</b> , 864-869 (1925).
Isomerization of pinene.	Pd black.	Richter and Wolff: <i>Ber.</i> , <b>59</b> 1733-1736 (1926).
Isomerization of pinene to camphene; T. 10°; yield, 80% monoterpenes.	Florida earth, or 40% Japanese acid earth.	Kuwata: <i>J. Soc. Chem. Ind. Japan (Suppl.)</i> , <b>32</b> , 372B (1929).
Isomerization of pinene and nopinene to camphene; T. 90°.	Water or acid treated bleaching earth, washed and dried at high temp.	Shering-Kahlbaum A.-G.: F.P. 704,461 (1930).
Isomerization of nopinene to pinene; T. 150°.	Bleaching earth, ton pieces, or fuller's earth pretreated with acid and water.	Shering-Kahlbaum A.-G.: F.P. 704,809 (1930).
Isomerization of pinene to camphene; isomerization velocity higher than polymerization velocity; therefore it is suggested discontinuing the reaction at a certain point to obtain a terpene mixture with camphene predominating; yield, 56-62%.	Acid ton (ton heated with 10% HCl for 6 hrs.); 0.5 g. of the catalyst used.	Tischtschenko and Rudakow: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>6</b> , (69) (1933).
Isomerization of pinene to dipentene and terpinene; (1) T. 70-100°; (2) T. 125-150° with stirring; pressure, 4-5 atm.  e.g., 2000 g. $\alpha$ -pinene; T. 75°; time, 4 hrs. with stirring; yield, 85% dipentene and 12% terpinole; the third product not identified.	(1) 5-15% H <sub>3</sub> PO <sub>4</sub> ; (2) 65-75% H $\cdot$ COOH or 90-100% CH <sub>3</sub> COOH; solvents such as gasoline, benzene, or toluene may be present. 325 g. 70% H <sub>3</sub> PO <sub>4</sub> .	
Isomerization of 1-linalool to geraniol in addition to dehydration, ring formation and polymerization take place; T. 159°.	10% Japanese acid earth.	Ono and Takeda: <i>Bull. Chem. Soc. Japan</i> , <b>2</b> , 16 (1927).
Isomerization of 200 g. geraniol to linalool; T. 225°; time, 21 hrs. duration of the reaction.	40 g. active charcoal.	Kimura: <i>Bull. Chem. Soc. Japan</i> , <b>10</b> , 530 (1935).
Isomerization of terpene alcohols; ring closure.	W acids; alkali metals; Pt, Pd, Ni, Cu, Fe, Co hydroxides; organic acid salts or carbonates of alkalis or alkaline earths; halide cpds. of Al, Hg, Bi, Zn, Sn, Fe; alumina, silica gel, active charcoal.	Kyokai: Japan P. 98,967, Jan. 11, 1933.
Isomerization of olefinic phenols: eugenol to isoeugenol (double bond shift); T. 300°.	Platinized charcoal.	Lewina: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , <b>6</b> , 1092 (1936).
Isomerization in addition to polymerization of terpene hydrocarbons.	Floridin or activated bleaching earths.	Gurwitsch: <i>Z. physik. Chem.</i> , <b>107</b> , 235 (1923).
Isomerization of aliphatic tetrahydroterpene.	Alkalies and acids.	Zelinsky and Lewina: <i>Ber.</i> , <b>62</b> , 1861-1863 (1929).

Table 10 (Continued).

Reaction	Catalyst	Observer
Isomerization of cyclohexylidene acetone and cyclohexanyl acetone; conversion of isopulegone by alcoholic $\text{H}_2\text{SO}_4$ to pulegone whose properties differ from those of pure pulegone; isopulegone readily isomerized by Na ethylate so that its velocity cannot be measured; by oxidation of pulegone with $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{H}_2\text{SO}_4$ , isopulegone originates and isomerization does not occur.	Oxalic acid acts more slowly than $\text{HCl}$ , and the latter causes an action opposite to that of $\text{H}_2\text{SO}_4$ .	
Isomerization of <i>l</i> -menthone (terpenic ketone) to isomeric <i>d</i> -menthone; T. $220^\circ$ ; time, 20 hrs.	50% active charcoal.	Kimura: <i>Bull. Chem. Soc. Japan</i> , <b>10</b> , 330 (1935).
Isomerization of 1-menthene to 3-menthene (of commercial value).	Silicic acid gel.	

## Catalytic Cyclization (Aromatization)

Table 1. Catalytic Cyclization or Aromatization of Organic Compounds.

Reaction	Catalyst	Observer
Cyclization of rubber to rubber of a semi-colloidal character giving solutions of low viscosity.	$\text{HCl}$ , $\text{H}_2\text{SO}_4$ .	Geiger: <i>Helv. Chim. Acta</i> , <b>9</b> , 549 (1926). Kirchhof: <i>Kautschuk</i> , <b>1</b> , (1926). Staudinger and Bondy: <i>Ann.</i> , <b>468</b> , 1 (1929).
Cyclization in the polymerization of phenylbutadiene to $\text{CCl}_4$ with elimination of some of the double bonds; T. greater than $200^\circ$ .	$\text{SnCl}_4$ .	Staudinger and Ashdown: <i>Ber.</i> , <b>63</b> , 717 (1930).
Cyclization of terpene aldehydes: 100 g. citronellal to isopulegol (citronellal added drop by drop to the catalyst suspension); T. $10^\circ$ ; isopulegol may be formed also in ether solutions, but then the amount of high-boiling polymerization products is considerable.	10 g. Japanese acid earth suspended in 100 g. $\text{CH}_3\text{OH}$ .	Kuwata: <i>J. Soc. Chem. Ind. Japan (Suppl.)</i> , <b>34</b> , 703 (1931).
Cyclization in isomerization and dehydrogenation of <i>n</i> -heptane to mono- and bicyclic paraffins.	$\text{AlCl}_3$ .	Nenitzescu and Dragen: <i>Ber.</i> , <b>66</b> , 1892 (1933).
Cyclization (intramolecular condensation instead of intermolecular polymerization).		Ziegler: <i>Ber.</i> , <b>67</b> , 139 (1934). Ziegler: <i>Ann.</i> , <b>513</b> , 43 (1934).
Cyclization of citronellal (300 g.) to isopulegol and diisopulegol and some terpene hydrocarbons; T. $135^\circ$ .	60 g. active charcoal.	Kimura: <i>Bull. Chem. Soc. Japan</i> , <b>10</b> , 330 (1935).
Cyclization of 1-pentene, 2-pentene and isopropyl ethylene; T. $-80^\circ$ ; polymerized products contain high-boiling cyclic hydrocarbons with increasing number of rings.	$\text{AlCl}_3$ .	Waterman, Leendertse and Tuleners: <i>Rec. trav. chim.</i> , <b>53</b> , 715 (1934). Waterman, Leendertse and Tuleners: <i>Inst. Petroleum Tech.</i> , <b>21</b> (145), 952-958 (1935).
Cyclization in the preparation of polycyclic cpds.	$\text{AlCl}_3$ .	Cook and Hewitt: <i>J. Chem. Soc.</i> , <b>1933</b> , 1098; <b>1936</b> , 62. Cook and Haslewood: <i>Ibid.</i> , <b>1935</b> , 767.
Cyclization of hydrocarbons of the fatty acid series; direct cyclization not dependent on the initial splitting of molecules; structure of aromatic hydrocarbons formed from paraffins and olefins depends wholly on the structure of the initial aliphatic hydrocarbons; T. $460-470^\circ$ .	$\text{Cr}_2\text{O}_3$ ; $\text{MoS}_2$ (for experiments with <i>n</i> -octane); $\text{ZnO}$ , $\text{Al}_2\text{O}_3$ , $\text{ThO}_2$ , Ni chromate, uranium oxide and fluoride, inactive.	Moldawski and Kamuscher: <i>Doklady Akad. Nauk. U.S.S.R.</i> , <b>1</b> , 355-359 (1936).

Table 1 (Continued).

Reaction	Catalyst	Observer
Cyclization of aliphatic hydrocarbons; e.g., <i>n</i> -octane to 60–94% by weight of aromatics, consisting of 85–90% <i>o</i> -xylene, 10% ethyl benzene and <i>m</i> - and <i>p</i> -xylene; T. 460–470°.	Cr <sub>2</sub> O <sub>3</sub> .	Moldawski, Kamuscher and Kobylskaja: <i>Zhur. Obshchei Khim. (U.S.S.R.)</i> , 7 (69) 169–178 (1937).
Cyclization of low molecular weight hydrocarbons: (1) <i>n</i> -heptane to 26% aromatics and 8% olefins; (2) butylbenzene to 12% aromatics (naphthalene) and 12% olefins; (3) <i>n</i> -hexane to 17% aromatics and 10% olefins; (4) diisobutyl to 36% aromatics ( <i>p</i> -xylene) and 10% olefins; (5) octene to 43% aromatics ( <i>o</i> -xylene) and 49% olefins; (6) diisopropyl to 82% aromatics ( <i>m</i> -methylisopropyl benzene) and 9% olefins.		
Cyclization of 2-( $\beta$ ,1'-naphthyl-ethyl)- $\Delta^2$ -cyclopentenone to 1,2-cyclopentenonephenanthrene (C <sub>17</sub> H <sub>14</sub> ); T. 130°; unsaturated ketone remains unchanged at 130°, nor could it be converted into the expected 3'-keto-1,2,3,4-tetrahydro-1,2-cyclopentenonephenanthrene.	P <sub>2</sub> O <sub>5</sub> .	Harper: <i>J. Chem. Soc.</i> , 1937, 1859.
	H <sub>3</sub> PO <sub>4</sub> , syrupy.	
	AlCl <sub>3</sub> (in benzene or nitrobenzene).	Cohen and Cook: (Refer to C. 1936 I 2926); <i>J. Chem. Soc. (London)</i> , 1935, 1570–72.
Cyclization of aliphatic to cyclic hydrocarbons; T. 400–700°; contact time 6–50 sec.; pressure, 0.7–7.0 atm.	Carriers: Al <sub>2</sub> O <sub>3</sub> , MgO, bauxite, montmorillonite, bentonite, quartz, glauconite impregnated with oxides of V, Nb, Ta (2–5%).	Universal Oil Products Co.: Ital. P. 351,078, May 15, 1937.
Cyclization of hexane to benzene; T. 510°; contact time, 17 sec.; yield, 48%.	Al <sub>2</sub> O <sub>3</sub> impregnated with ammonium metavanadate.	Universal Oil Products Co.: Ital. P. 352,747, June 19, 1937.
Cyclization of heptane to toluene; T. 550°; yield, 48%; repetition of reaction gives a yield of 80%.	Cr, Mo, W, U.	
Cyclization of benzene: enrichment of light oils in aromatics to obtain benzene-benzene mixtures which are treated with H <sub>2</sub> SO <sub>4</sub> , and finely powdered K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ; added in portions in the cold with stirring; from a benzene containing 50% aliphatics, 15% olefins and 35% aromatics a product is obtained having 22% aliphatics, 7.5% olefins and 70.5% aromatics; loss, only 2%.	H <sub>2</sub> SO <sub>4</sub> , finely powdered. K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> .	Universal Oil Products Co.: F.P. 825,207, Feb. 25, 1938.
Cyclization of benzene in vapor phase; T. 500°; contact time, 3–20 sec.	Calcined MgO impregnated with PbCrO <sub>4</sub> and ZnSO <sub>4</sub> (catalyst prepared by treating magnesia at 800° with a 5% K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> solution, drying at about 300°, treating with 7.5% Pb acetate solution, drying at 300° and impregnating with a 25% solution ZnSO <sub>4</sub> and dehydrating first at 300° and then at 600°).	Universal Oil Products Co.: Ital. P. 352,497, June 11, 1937. F.P. 825,206, Feb. 25, 1938.
Cyclization in the formation of naphthalene from $\alpha$ - and $\beta$ -methylhydrindene, $\alpha$ - and $\beta$ -ethylhydrindene, $\alpha$ -isooctylhydrindene and methylisopropyl-hexahydrofluorene; reaction accompanied by scission of one of the C—C bonds in a five-member ring with subsequent cyclization to a six-member ring accompanied by dehydrogenation and/or dealkylation.	Se.	Egloff: "Reactions of Pure Hydrocarbons," p. 687, Reinhold Publishing Corp., 1937.

Table 1 (Continued).

Reaction	Catalyst	Observer
Cyclization in the transition of aliphatic terpenes to cyclic terpenes.		Staudinger and Widmer; <i>Helv. Chim. Acta</i> , 9, 529 (1926).
Cyclization and hydrogenation of hexadecane to saturated and condensed hydrocarbons; T. 500–600°C.; pressure, 3–9 kg./sq.cm.	None.	Gault and Bergmann; <i>Ann. combustibles liquides</i> , 1, 77 (1926). Gault and Bergmann; <i>Chimie &amp; industrie</i> , 16, 242 (1926).
Cyclization of benzines in vapor phase; T. 450–650°; most suitable, T. 495–540°; contact time, 2–20 sec.	Precipitated and calcined $\text{Al}_2\text{O}_3$ containing 5–10% $\text{H}_2\text{O}$ corresponding to the monohydrate $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ; when natural $\text{Al}_2\text{O}_3$ minerals are used, such as diaspor, bauxite, gibbsite, the sulfates, chlorides, or nitrates present must be removed.	Universal Oil Products Co.; F.P. 826,189, March 24, 1938.
Aromatization of paraffinic hydrocarbons; the products originating with catalyst (2) differ from those obtained with catalyst (1); solid paraffin from Rumanian crude oil corresponds to pentacosan, $\text{C}_{25}\text{H}_{52}$ containing 0.98% unsaturated products (iodine no. according to Galle, 1.25) were treated at ordinary pressure and comparatively low temp. (200–250°); thereby paraffin hydrocarbons, aromatized hydrocarbons (benzene and toluene) and small amounts of naphthenes were obtained; the paraffinic hydrocarbons consist chiefly of those with branched chains, i.e., the aromatics of benzene and toluene; as result of strong polymerization, an asphaltic mass of complex hydrocarbons, $\text{AlCl}_3$ and $\text{AlCl}_3 + \text{C}$ is left, which decomposes with water with formation of heavy, unsaturated oily products; the formation of aromatic hydrocarbons is explained by (1) intermediary formation of cycloparaffins formed from olefins by action of $\text{AlCl}_3$ (the olefins originate in the reaction besides paraffin hydrocarbons); the naphthenes are then perhaps dehydrogenated by the action of nascent $\text{AlCl}_3$ ; (2) by cyclization of paraffin hydrocarbons with branched chain to naphthenes and their conversion by dehydrogenation into aromatic hydrocarbons; and (3) by cyclization of <i>n</i> -paraffin and subsequent dehydrogenation; the paraffinic hydrocarbons forming paraffin under the influence of $\text{AlCl}_3$ and nascent $\text{H}_2$ undergo splitting, reduction, polymerization, isomerization, and cyclization.	(1) Anhydrous $\text{AlCl}_3$ acts differently from (2) $\text{AlCl}_3$ obtained <i>in statu nascenti</i> (when $\text{AlCl}_3$ is formed in the mass of the product upon which it must react) because in the latter case $\text{AlCl}_3$ is formed in a very finely divided state and with great reaction ability; and simultaneously nascent hydrogen participates with great energy in the reaction; $\text{AlCl}_3$ and nascent $\text{H}_2$ obtained by action of $\text{HCl}$ on activated $\text{Al}$ .	Otin and Dima; <i>Refiner Natural Gasoline Mfr.</i> , 17, 283–288 (1938).
Aromatization of hydrocarbons; aliphatic hydrocarbons with 6–12 C atoms are treated at 400–700° (best 500°) over the catalyst for a maximum of 10 seconds, e.g., from heptane about 31% of toluene is obtained; with single catalysts, only 20–22% toluene is obtained.	Equal amounts of $\text{Cr}_2\text{O}_3$ and $\text{Mo}_2\text{O}_3$ precipitated on active alumina; (2) $\text{Cr}_2\text{O}_3$ and $\text{V}_2\text{O}_5$ on active alumina; (3) $\text{Mo}_2\text{O}_3$ and $\text{V}_2\text{O}_5$ on active alumina; (2) and (3) give equal yields of toluene. $\text{Cr}_2\text{O}_3$ or $\text{Mo}_2\text{O}_3$ .	Universal Oil Products Co. (Grosse and Morrell); U.S.P. 2,157,204, 2,157,940, and 2,157,941, May 9, 1939.
Cyclization (aromatization) of aliphatic hydrocarbons: <i>n</i> -pentane, <i>n</i> -hexane, 2-methylpentane, <i>n</i> -heptane, 2-methylhexane, <i>n</i> -octane, 3-methylheptane, 2,2,4-trimethylpentane, <i>n</i> -nonane, <i>n</i> -hexane-1, <i>n</i> -hexene-2, <i>n</i> -heptene-1, <i>n</i> -heptane-2, <i>n</i> -octene-2, cyclohexane, methylcyclohexane and cyclohexene are led over the catalyst at 465° and under atmospheric pressure with a contact time of 20 sec.; the chain branching may increase or decrease the aromatization tendency; in the aromatization of olefins, the extent of conversion depends essentially on the position of the double bond in the molecule; besides the formation of lower aromatics caused by cracking, aromatization proceeds as a simple ring closing reaction without isomerization of the carbon skeleton; the secondary carbon atoms favor ring closure.	$\text{Cr}_2\text{O}_3$ (under conditions used, it catalyzes the displacement of the middle olefinic double bonds).	Hoog, Verheus and Zuiderweg; <i>Trans. Faraday Soc.</i> , 35, 993–1006 (1939).

Table 1 (Continued).

Reaction	Catalyst	Observer
Cyclization of aliphatic hydrocarbons, <i>e.g.</i> , <i>n</i> -heptane is completely aromatized under special conditions at 468°; under other conditions olefins, as well as a considerable amount of saturated hydrocarbons which make up about 25% of the liquid reaction product; using ThO <sub>2</sub> as a catalyst, only saturated hydrocarbons are obtained at 468°; the same takes place when using Al <sub>2</sub> O <sub>3</sub> gel, but at 540°; over-activated Al <sub>2</sub> O <sub>3</sub> at same temp. promotes the formation of 16% olefins and 2% aromatics in addition to saturated hydrocarbons; with an increase in temp., cracking reactions become more pronounced.	Cr <sub>2</sub> O <sub>3</sub> and Cr <sub>2</sub> O <sub>3</sub> gel (during the reaction, poisoning effects are observed by treatment with O <sub>2</sub> -containing gases; at the reaction temp., the catalyst may be regenerated); gel-like catalysts should not be overheated; water which is strongly adsorbed by the catalyst appears to be an effective poison in the conversion. ThO <sub>2</sub> . Al <sub>2</sub> O <sub>3</sub> gel. Activated Al <sub>2</sub> O <sub>3</sub> .	Taylor, H. S. and Turkevich: <i>Ibid.</i> , 35, 921-33 (1939).

# Chapter 11

## Catalysis in the Petroleum Industry

### Introduction

Since the petroleum industry has been revolutionized by catalytic processes, it has been chosen for detailed description as an example of an industry in which catalysis plays a major role. From the catalytic viewpoint, the petroleum industry today is concerned principally with the production of high-octane motor fuels and lubricating oils; but in the future, individual synthetic hydrocarbons, such as benzene, toluene, xylenes, monoolefins and diolefins, acetylene and others used in the production of explosives, dyes, medicinals, pharmaceuticals, perfumes, synthetic rubber, plastics, resins, and many other products, will assume great importance.

The world petroleum industry has an investment of approximately 20 billion dollars and a production of about 2 billion barrels of crude oil per year, from which are produced approximately 800 million barrels of motor fuel. More than one-half of this crude oil and motor fuel is produced in the United States and is used largely for the operation of its 30 million motor cars. The growth of the industry can best be evaluated by the consumption of motor fuel, which has increased approximately five-fold within the past two decades.

The increased production of motor fuel has been made necessary by the extremely rapid growth of the motor industry, and the demand for motor fuel has brought about the development of the cracking process to supply additional yields of gasoline from the relatively limited supplies of crude oil. How well the cracking process has accomplished its purpose is indicated by the fact that the output of gasoline by cracking is more than equal to that produced by distillation of the gasoline contained naturally in the crude oil (*i.e.*, about 55 per cent of the total gasoline production from crude oil), which results in a saving of over 1,400,000,000 barrels of crude oil per year in the United States alone.

Coincident with the production of cracked gasoline resulting from the pyrolytic or thermal treatment under pressure of the higher-boiling fractions of petroleum, about 350 billion cubic feet of cracked gases are made yearly. These are now being converted commercially in part into polymer gasolines, alkylates, and iso-octanes. The gases from cracking contain a high percentage of olefin hydrocarbons, the conversion of which into alcohols, glycols, ethers, esters, ketones, amines, chlorinated and nitrated derivatives, aldehydes, synthetic lubricants, resins, rubber and plastics generally have challenged the skill and inventiveness of the chemist.

Success with the relatively reactive olefin hydrocarbons has led to a study of reactions with the comparatively inert paraffinic hydrocarbons,

particularly by catalytic methods, and the mass attack upon these problems has resulted in commercially adaptable methods which allow conversion of practically all types of hydrocarbons into any other types, depending upon which is the most desirable for the objectives and purposes sought.

In general it may be stated that any type of hydrocarbon can be converted into any other type by catalytic reactions already established and which are adaptable to commercial production. Thus the foundation has been laid for an improved petroleum industry and for a synthetic chemical industry utilizing petroleum as a raw material for the production of a myriad of synthetic products referred to above, which heretofore have been known only as coal-tar derivatives. Dehydrogenation, polymerization, depolymerization, alkylation, isomerization, hydrogenation, cyclization—these are some of the methods by which these products may be obtained catalytically. Simultaneous with the production of commodities useful to mankind has been the development of a hydrocarbon chemistry which has furnished chemists with tools heretofore unknown for investigation of hydrocarbon reactions.

The complexity of hydrocarbon chemistry may be simply illustrated by the following table showing the possible number of paraffin isomers corresponding to each individual hydrocarbon:

Table 1.

Number of Carbon Atoms in the Molecule	Number of Isomers Aliphatics $C_nH_{2n+2}$	Number of Carbon Atoms in the Molecule	Number of Isomers Aliphatics $C_nH_{2n+2}$
4	2	14	1,858
5	3	15	4,347
6	5	16	10,359
7	9	17	24,894
8	18	18	60,523
9	35	19	147,284
10	75	20	366,319
11	159	25	36,797,588
12	355	30	4,111,846,763
13	802	40	62,491,178,805,831

The entire field of hydrocarbon power fuels, in which may be included petroleum, natural gas and coal, is encompassed by the reactions of hydrocarbons. The interchangeability and substitution of one natural hydrocarbon resource by another guarantees a continuing supply of motor fuel and hydrocarbon derivatives and provides the stimulus for the development of new fields in hydrocarbon chemistry. Petroleum resources estimated to be 20,000,000,000 barrels of crude oil (April, 1940) for the production of hydrocarbons and their derivatives may be supplemented by approximately 75 trillion cubic feet of natural gas and 7,400 billion tons of coal. These materials may be converted into hydrocarbons of any desired type or even any desired individual hydrocarbon by reactions already established. The petroleum industry employs about 5,000 research workers expending about \$20,000,000 a year.

During the past decade interest in hydrocarbon research has been greatly stimulated in our universities and in the National Bureau of Standards by financial grants for fundamental research. The projects under these grants initiated a definite and widespread interest in hydro-

carbon research which has continued because of the large economic possibilities and intrinsic scientific values to be found in hydrocarbon chemistry and in the petroleum industry.

### A. HIGH-OCTANE MOTOR FUELS

#### Pyrolysis of Gaseous Hydrocarbons

The particular catalytic hydrocarbon processes which have been selected as typical of developments in the petroleum industry illustrate the trend whereby groups of individual hydrocarbons occurring in tremendous quantities may be converted into other hydrocarbons which are more reactive and more desirable because of the products and derivatives which can be made therefrom. In this sense the catalytic developments in the petroleum industry furnish the basis for the development of superior motor fuels on the one hand, and for raw materials for the chemical industry to make more valuable products on the other hand.

Generally, the preponderant supply of lighter hydrocarbons in petroleum, natural gas, etc., is paraffinic in character, and for both motor fuel use and the production of chemical derivatives it is desirable to convert them into the more active types, namely, diolefins, olefins, and aromatics. As a background for the development of these catalytic processes a brief resume of the reactions involved in the pyrolysis of hydrocarbons will be given.

Processes involving the cracking of normally gaseous hydrocarbons have received impetus from the fact that they are available in enormous quantities and that, by this simple method of pyrolytic treatment, compounds of greater activity and increased value are obtained. Thus from methane, which is the chief constituent of natural gases, it is possible to produce acetylene and ethylene. Ethane may be made to produce large quantities of ethylene, and by properly controlling and limiting the time of exposure to pyrolytic conditions, propane and butanes may be made to yield substantial quantities of the corresponding quantities of propene and butene, which have a high reactivity and many practical uses.

Methane, the chief constituent of natural gas, produces only fair yields of acetylene and ethylene by pyrolysis at  $1120^{\circ}$  and contact time of 0.1 second. Ethane begins decomposition in the absence of catalyst at about  $485^{\circ}$ , producing principally ethylene and hydrogen over a range of several hundred degrees beyond this. At higher temperatures methane, acetylene, and aromatic hydrocarbons are also formed.

The principal products from propane at  $650^{\circ}$  are propene and hydrogen. Other products are methane, ethane, acetylene, and butanes. At  $725^{\circ}$  the yield of propene decreases, and that of ethylene increases.

As in the case of other hydrocarbons, butanes correspond to simple primary dehydrogenation reactions at  $540$ – $595^{\circ}$  and  $700$ – $1000$  pounds per square inch pressure, producing about 40 per cent butenes. Higher temperatures give lower yields of butenes. The pyrolysis of butanes to form butenes is important in the production of polymer motor fuels.

More extensive decompositions involve the splitting of both the ter-



minal and middle C—C bonds to form respectively methyl, propyl, and ethyl radicals, which may enter into further reactions with the unchanged butanes. The pyrolysis of butanes under conditions conducive to the formation of relatively high yields of butenes is important in the production of aviation fuels consisting of mixtures of octanes of high antiknock rating, since the butenes may be catalytically polymerized to octane dimers and then hydrogenated to produce the mixtures of octanes.

Methods for the production of ethylene from higher hydrocarbons, with temperatures of 565–620°, subject to atmospheric pressure and time less than 0.1 second, yielding 40 per cent ethylene, and for the production of acetylene by pyrolysis of other hydrocarbons, have been developed. Similarly, high yields of ethylene and other olefins, as well as diolefins, have been shown by many workers.

Since the gas from the cracking process plays such an important role in various catalytic processes, typical analyses are shown in Table 1.

Table 1. Some Analyses of Gases from the Cracking Process.  
(Per Cent by Volume)

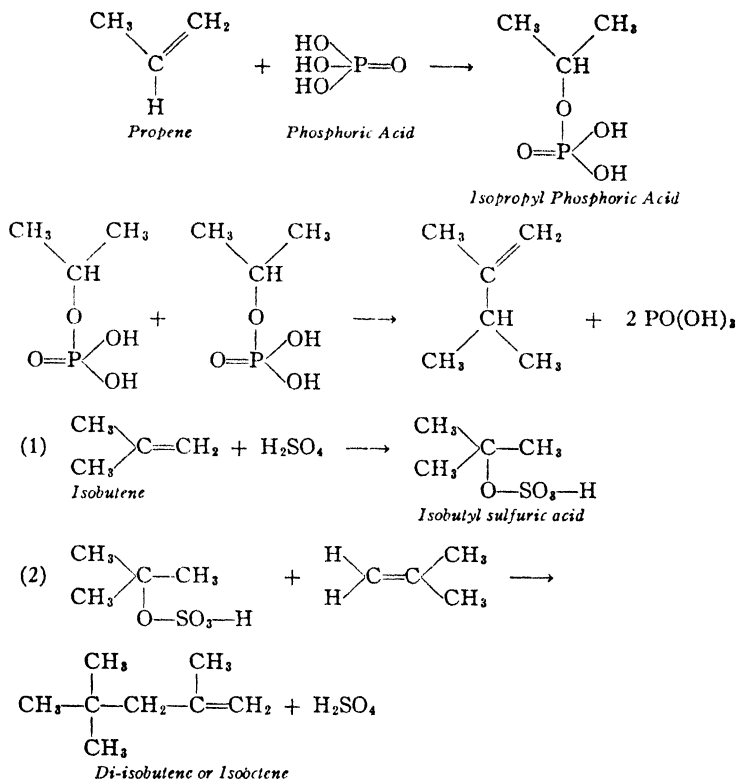
Charging Stock	Receiver Gas	Stabilizer	Reflux	Stabilizer	Gas
Hydrogen (non-Condensables)	4.3	0.1	4.1	0.6	Trace
Methane	22.2	0.1	—	3.4	—
Ethylene	6.0	0.6	—	16.0	1.1
Ethane	17.3	3.2	—	17.8	9.4
Propene	11.2	16.6	11.8	29.0	18.9
Propane	26.8	16.8	28.8	22.2	47.1
<i>n</i> -Butenes	4.0	20.2	11.6	4.9	7.6
<i>i</i> -Butene			8.3		3.9
<i>i</i> -Butanes	5.6	40.5	35.4	2.0	11.1
<i>n</i> -Butane			—		
Butadienes	—	—	—	2.0	—
Pentane	0.2	1.2	—	0.2	—
CO <sub>2</sub> + Nitrogen	1.6	0.5	—	0.4	—
Hydrogen sulfide	0.8	—	—	0.2	—

### Catalytic Polymerization

Polymerization of olefinic hydrocarbons, one of the most important of catalytic reactions, may be effected by heat alone, by the action of actinic light, by mineral acids, and by many metal salts. In the polymerization of ethylene, some difficulty is experienced in limiting the extent of the reaction to the formation of low-boiling products. Propene and butenes are controllably polymerizable by the use of either sulfuric or phosphoric acids; and in mixtures containing isobutene, normal butenes, and propene, the hydrocarbons may be removed in successive steps by the use of selected conditions of temperature, and time of contact with catalysts or conditions may be controlled so as to favor mixed or cross polymerization, for example, between normal and isobutenes, to form high yields of isomeric octenes which may be hydrogenated to octanes of high antiknock value.

The polymerization reaction may be illustrated by the Ipatieff catalytic process employing the so-called solid phosphoric acid. This process is widely used for the commercial production of high-octane polymer gasoline and iso-octane.

The chemistry of the polymerization reactions may be illustrated by the following equation showing the reactions of propene and phosphoric acid on the one hand and isobutene and sulfuric acid on the other.



Similar reactions could be shown with the butenes and phosphoric acid on one hand, and sulfuric acid and propene on the other.

The ever increasing demand for high-compression antiknock motor fuels and the large amount of hydrocarbon gases available, and which are burned for fuel, stimulated the development of polymerization processes. The volume of polymer gasoline which may be obtained yearly from all sources is estimated to be almost one-half of the motor fuel now being produced from other sources. Based upon present operations (1940) the yield or production of polymer gasoline will exceed 50 million barrels per year.

Polymer gasoline can be made by the thermal treatment at temperatures of from 500–700° and pressures varying from atmospheric to several thousand pounds per square inch. This process does not give the maximum conversion. With catalytic polymerization for the treatment of gaseous olefinic hydrocarbons comprising, *e.g.*, the higher olefins, such as propene and butenes, practically theoretical yields of olefins may be obtained at temperatures of 200° and 400 pounds or higher pressure per square inch. The polymer gasoline has an octane rating of 80 and on a blending basis up to

135, depending upon the gasoline with which it is blended and the percentage.

Selective polymerization employs about 150° and 700 pounds per square inch and utilizes the normal and isobutenes present in cracked gases for the production of isoöctenes. The isoöctenes have an octane rating of 84 and, on blending, a value in excess of 150. The isoöctanes produced by hydrogenation have octane ratings of from 95 to 98 and individual octanes have values in excess of 100. Isoöctane gasoline is of extreme importance in aviation, both for commercial and military planes. The isoöctanes are blended with lower-boiling petroleum fractions for starting, and a small amount of ethyl fluid to raise the octane value to 100. An improvement in power output of 30 per cent is shown with 100-octane fuel compared with 87-octane. The saving in pay load for large commercial transports may be several thousand dollars. Millions of barrels of isoöctane are produced currently per year with ever increasing amounts for the needs of military aviation.

The variation in isomeric forms of hydrocarbons which becomes practically infinite in the high molecular weight paraffin hydrocarbons is quite evident even with the octanes as is shown in Table 2.

Table 2. Octanes.

	M. P. (°C.)	B. P. (°C. at 760 mm.)	Density $\rho_4^{20}$
$C_8H_{18}$ , <i>n</i> -Octane	- 56.82	125.68	0.70256
2-Methylheptane, isoöctane	-111.3	117.2	0.6980
3-Methylheptane		119.0	0.7054
<i>d</i> ,3-Methylheptane		117.0	0.712
1,3-Methylheptane		115.0	
4-Methylheptane		118.0	0.7165
3-Ethylhexane		118.6	0.7128
2,2-Dimethylhexane		106.9	0.6953
2,3-Dimethylhexane		115.8	0.7118
1,2,3-Dimethylhexane		113.5	
2,4-Dimethylhexane		109.8	0.7030
<i>d</i> ,2,4-Dimethylhexane		111.5	0.704
1,2,4-Dimethylhexane		110.5	0.704
2,5-Dimethylhexane	90.7	109.40	0.69378
3,3-Dimethylhexane		111.3	0.710
3,4-Dimethylhexane		117.9	0.7193
2-Methyl-3-ethylpentane		114.0	0.7030
3-Methyl-3-ethylpentane	- 90.9	118.4	0.7270
2,2,3-Trimethylpentane		110.1	0.7173
2,3,3-Trimethylpentane	-119.1	114.6	0.7253
2,2,4-Trimethylpentane	-107.41	99.3	0.6918
2,3,4-Trimethylpentane		113.8	0.7194
2,2,3,3-Tetramethylbutane	102.2	106.5	

The antiknock value of various octanes is shown in Table 3.

Approximately 100 polymerization units have been installed throughout the world to date (1940), varying in capacity from 125,000 to 27,000,000 cubic feet of cracked gas per day. The charge, which is delivered from the stabilizer of the cracking unit at a pressure of approximately 50 to 200 pounds, is compressed from 200 pounds up to 1000 pounds to the operating pressure of the polymerization process. The charge is passed to a heater where the temperature of the gas is raised to the order of 180–205° and is

Table 3. Antiknock Value.

	Octane Number
n-Octane	-28.0
3-Methylheptane	34.5
2,5-Dimethylhexane	52.0
2,3-Dimethylhexane	75.5
3,4-Dimethylhexane	84.5
3-Methyl-3-ethylpentane	90.5
2,2,4-Trimethylpentane	100.0
2,2,3-Trimethylpentane	101.0
2,2,3,3-Tetramethylbutane	103.0

then passed in series through tubes filled with solid phosphoric acid catalyst, where the polymerization reaction occurs. The polymer product leaving the last catalyst vessel is cooled to a temperature of 75° and discharged directly into the stabilizer, where the polymer, together with the amount of butanes required to give the desired amount of pressure, is separated from the remainder of the gas referred to as "spent gas." A diagrammatic flow diagram of the polymerization process is shown in Fig. 1. Fig 2. is a photograph of an experimental polymerization plant. Commercial polymerization plants are shown in Figs. 3 and 4.

Control of the operating conditions is automatic and is no more than that required from the ordinary refinery stabilizer or absorber. The arrangement permits cutting the polymerization plant in or out of the gas flow without interrupting the cracking plant stabilizing and gas disposal system. The pressures are regulated at the outlet of the catalyst tower and the polymerization plant stabilizer. By proper manipulation of various operating factors, high-olefin conversion and long catalyst life are obtained. In some refineries, where the olefin content of the cracked gas is high, a portion of the spent gas is recirculated with the fresh feed to control the temperature rise which takes place in the catalyst vessel, which if uncontrolled would yield a product having a high percentage of material boiling outside of the gasoline range. The spent gas from the polymerization unit is discharged to the refinery fuel system and the gasoline sent to storage. This spent gas could be catalytically dehydrogenated if desired, and the resulting olefins re-treated.

The gas from the stabilizer charged to the poly unit has a B.t.u. content of approximately 1700 per cubic foot, which is reduced to 1300 after polymerization of the olefins present. The reduction in volume of the stabilizer gas depends upon the olefin content of the charge, which generally ranges from 20 to 40 per cent, and for the average type of cracked gas a yield of approximately 6 gallons of polymer gas for 1000 cubic feet of cracked gas processed is obtained. A preferable charging stock for the polymerization process is the cracked gas obtained from the stabilizer of the cracking unit, which comprises about two-thirds of the polymerizable hydrocarbons produced in cracking. As the average quantity of stabilizer gas produced is generally about one-third of the total gas from cracking, economy in the plant size is effected by treating only the stabilizer gas. However, the total gas produced in cracking may be treated. As the catalyst loses activity, the temperature rise as a result of the reaction decreases, and hence, less recycle gas is used. This increases the olefin con-

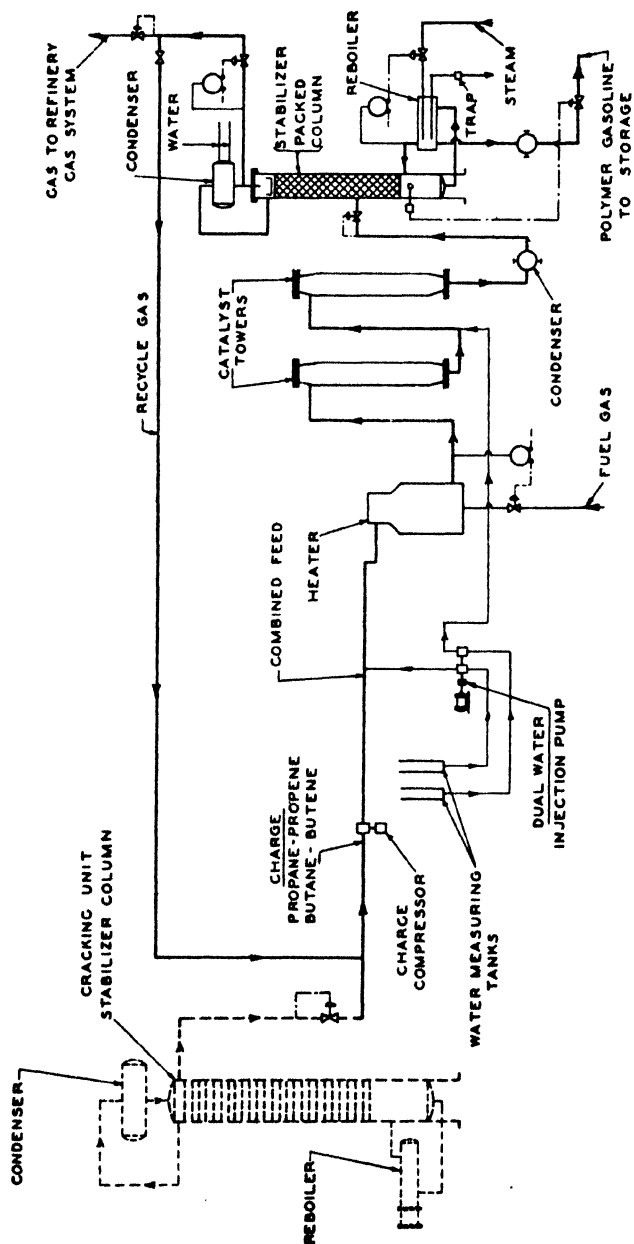


FIGURE 1.—Flow Diagram of Catalytic Polymerization Unit.

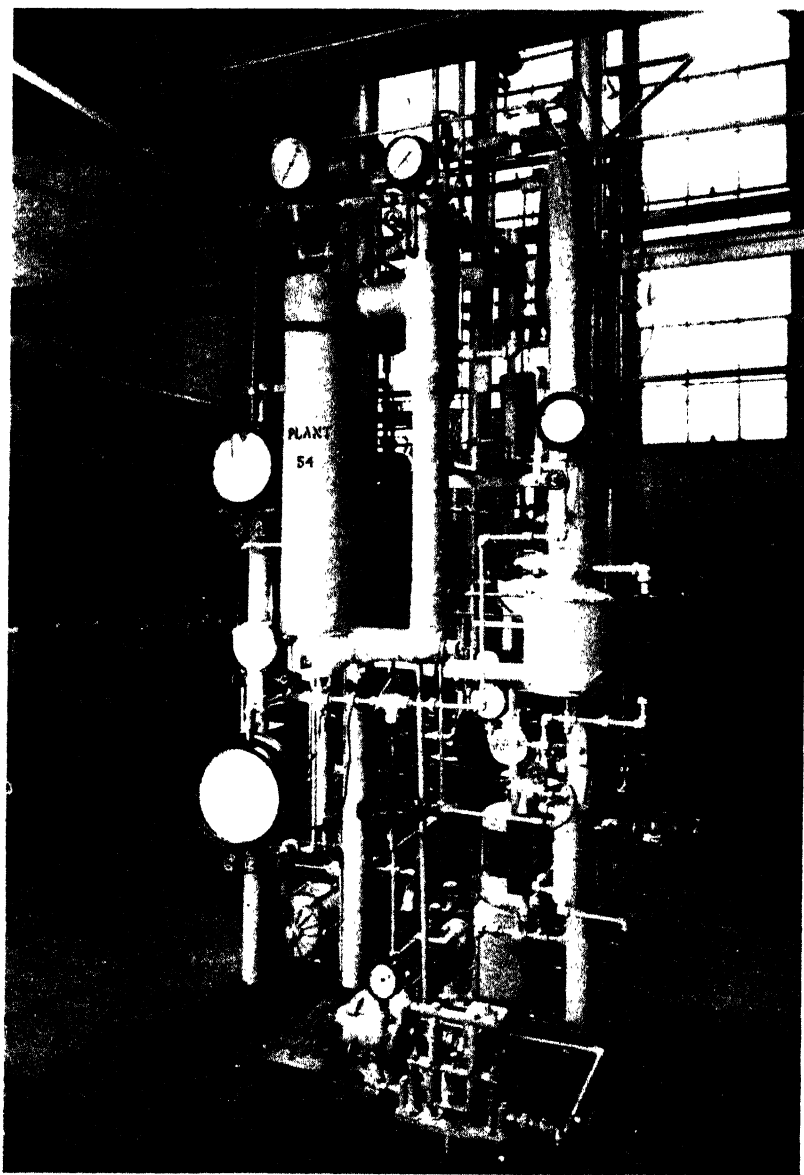


FIGURE 2.

tent of the combined feed and helps to maintain the required temperature in the catalyst bed. Yields of polymer gasoline per pound of catalyst have

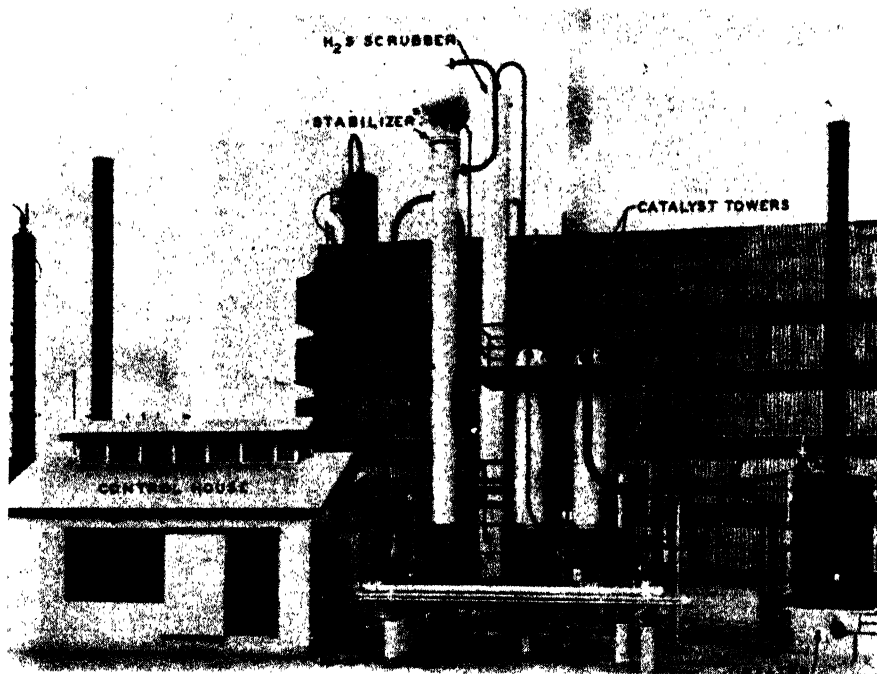


FIGURE 3.

been over 100 gallons, and catalyst life of over six months has been obtained.

As an example of the variation in composition of gases and yields of polymer gasoline, Table 4 is presented.

Table 4. Cracked Gas Analyses (Charging Stocks to Poly Units).

Poly Units	1	2	3	4	5
Composition (mol %)					
Hydrogen sulfide	0.15	1.8	0.33	1.0	0.35
Hydrogen	4.1	0.2	0.3	0.1	—
Methane	25.8	5.0	4.6	3.4	2.2
Ethylene	5.3	2.6	4.0	3.7	2.3
Ethane	16.9	18.9	20.3	16.4	10.7
Propene	15.0	17.1	17.9	23.4	17.8
Propane	23.3	44.1	29.5	27.8	25.1
<i>n</i> -Butenes	2.8	2.8	7.4	9.8	16.4
Isobutene	1.4	3.0	4.1	5.0	6.8
Butanes	4.6	5.9	11.9	10.0	17.9
Propene-Butenes	19.2	22.9	29.4	38.2	41.0
Poly gasoline (Gals. per 1000 cu. ft. gas)	3.7	4.4	6.1	7.6	9.5

It is preferable that hydrogen sulfide, amines, and other impurities be removed prior to treatment of the gases, and this may be accomplished by water and caustic washes, indicating that conversion increases within limits with increasing temperatures between 205° and 240°. The yield of

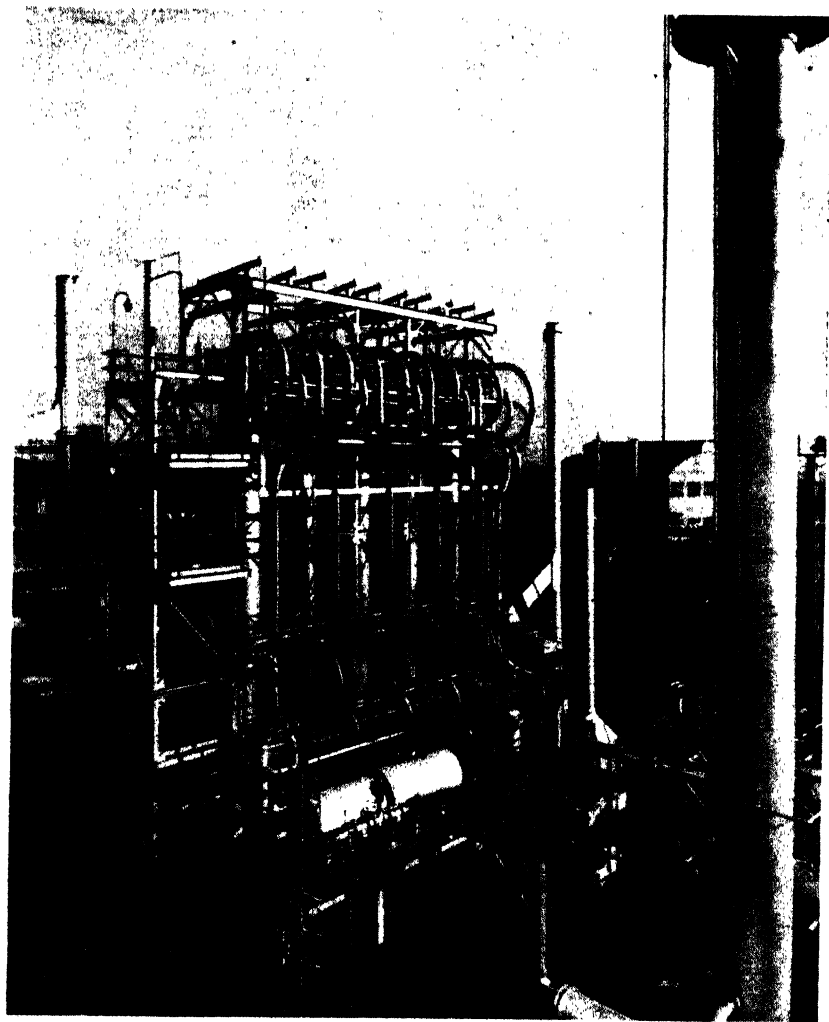


FIGURE 4.

polymer gasoline based on a 10-pound Reid vapor pressure varies between 4 to 9.4 gallons per 1000 cubic feet, depending upon the olefin content of the gas (the olefin conversion ranges between 85 and 95 per cent). The higher olefin conversions are for cracked gas containing higher olefin contents, for example, around 40 per cent. The polymer gasoline based upon the treatment of stabilizer gas falls within the full boiling range of regular motor gasoline, and in general has a low gum content and is otherwise satisfactory



for high antiknock gasoline or for blending stock. When the sulfur content of the gas is removed prior to conversion of the gas, the mercaptan content of the final product is zero; otherwise the resulting product may be sweet-

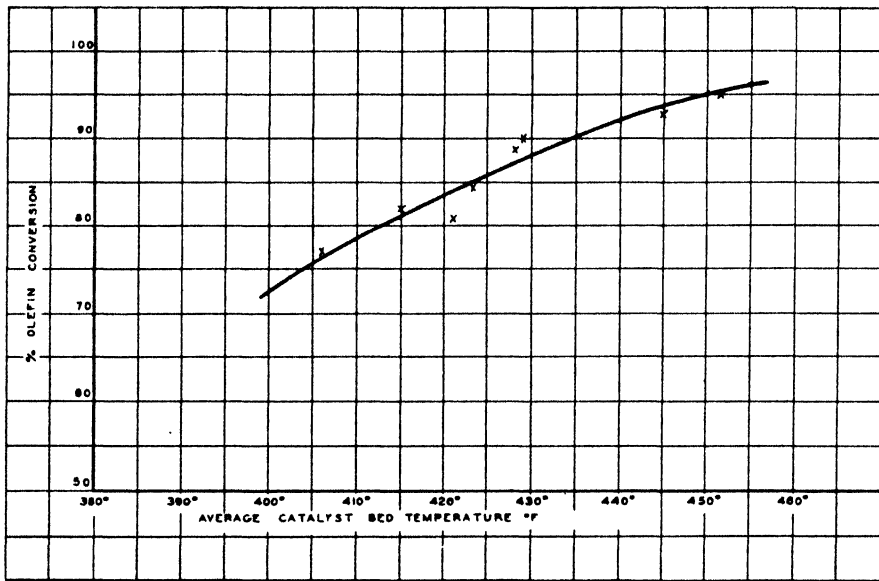


FIGURE 5.—Effect of Catalyst Temperature on Olefin Conversion.



FIGURE 6.

ened by the conventional caustic soda and /or plumbite treatment. Sweetening with copper salts may also be employed. In a balanced refinery operation, the yield of gasoline by polymerization may be increased over 3 per cent and the octane number over 3 units. The octane numbers of the

polymer gasolines vary from 80 to 84. Fig. 5 shows the effect of catalyst temperature on olefin conversion.

The polymerization process may be operated on either a non-selective or a selective basis. In the latter case the stock is selected so that the reaction is principally between isobutene and butenes to produce maximum yields of isoöctenes. The yield of isoöctenes can be controlled to 90-95 per cent with some heavier polymers and the octane numbers may vary between 95 and 97 after hydrogenation of the isoöctene to produce isoöctanes. Fig. 6 is a photograph of an isoöctane plant.

### Catalytic Hydrogenation

The isoöctenes produced may be converted into isoöctanes by the U.O.P. low-pressure hydrogenation process at pressures of about 75 pounds and temperatures of 160° in the presence of a nickel catalyst. The hydrogenation reaction is also exothermic; hence the unit is similar in design to the selective polymerization unit in the step of close temperature control by means of a water jacket around the reactor. A flow chart of the low-pressure hydrogenation unit is shown in Fig. 7. The properties of the hydrogenated isoöctanes are shown in Table 5.

Table 5. Isoöctanes.

Gravity (°A.P.I.)	66.4
100 cc. Distillation (A.S.T.M.)	
I.B.P. (°F.)	210
Per cent distilled over	
10	222
50	227
90	232
E.P. (°F.)	254
Octane No. (A.S.T.M. Motor Method)	95.0
Reid Vapor Pressure (lbs.)	1.6
Sulfur (%)	0.001
Olefins (%)	0.5
Gum (Copper Dish)	0
Color	30

The isoöctanes as produced are not aviation gasoline as such. They must be blended with aviation stock, such as special straight-run or natural gasoline, and isopentane for volatility.

The usual procedure for preparing 100-octane aircraft fuel is to blend commercial isoöctane with aviation straight-run gasoline and isopentane, and add 3 cc. of tetraethyl lead per gallon. The isopentane is used to supply the front-end volatility which isoöctane lacks. The amount of isopentane incorporated in the finished blend is usually 10-15 per cent, depending on its availability and also on the vapor pressures of the isoöctane and the straight-run base fuel.

Laboratory inspection data for several such blends and for the various components used to make up those blends are shown in Table 6. Ratings by both the Motor and the Army method are included. In the United States, the Army method is specified whereas the Motor method is used in England for 100-octane fuels. As indicated in the table, the Army ratings

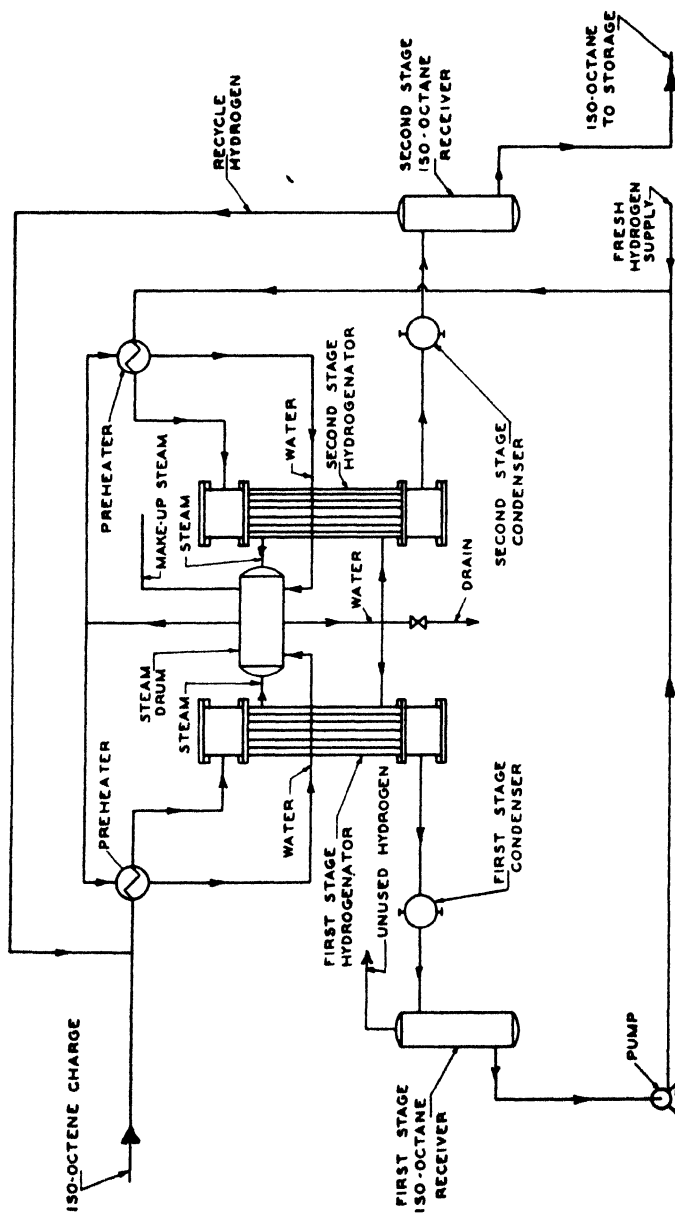


FIGURE 7.—Flow Diagram of U.O.P. Hydrogenation Unit.

for leaded blends of this sort are usually about 2 octane numbers higher than corresponding Motor-method values.

Based on the results given in Table 6, a commercial 100-octane (Army method) 7-pound vapor pressure blend could consist of 40 per cent of 95-octane isoöctane, 45 per cent of 74-octane aviation straight-run, and 15 per cent of 90-octane isopentane. To produce a similar blend to equal 100-octane by the Motor method, part of the straight-run would have to be replaced with isoöctane, for example, 45 per cent of isoöctane, 40 per cent of straight-run, and 15 per cent of isopentane.

Table 6. Laboratory Inspection and Antiknock Data for High-octane Aviation Blends.

	"A" U.O.P. Iso- octane	"B" Aviation Straight- Run	"C" Isopentane	Blends			
				50% A 50% B	40% A 50% B 10% C	40% A 45% B 15% C	50% A 40% B 10% C
Gravity (°A.P.I.)	66.4	66.7	95.7	66.5	68.6	69.6	68.7
100 cc. Distillation (A.S.T.M.)							
I.B.P. (°F.)	210	115	80	112	102	100	110
Per cent distilled over							
10	222	148	82	177	150	145	155
50	227	185	88	212	204	203	211
90	232	222	96	232	231	230	231
E.P. (°F.)	254	250	103	253	250	249	248
% Over	99.0	98.0	99.0	98.5	98.5	98.5	98.5
Reid Vapor Pressure	1.6	7.2	20.1	3.8	6.2	6.8	5.7
	Octane Number						
U. S. Army Air Corps Method							
Unleaded	95.0	74.0	90.0	84.0	84.0	84.5	85.5
+ 0.30 cc. TEL/gal.	100.0	—	—	—	—	—	—
+ 0.60 cc. TEL/gal.	—	—	100.0	—	—	—	—
+ 3.00 cc. TEL/gal.	—	91.0	—	99.5	99.5	100.0	100+
A.S.T.M. Motor Method							
Unleaded	95.0	73.5	90.0	84.0	84.0	84.5	85.5
+ 0.35 cc. TEL/gal.	100.0	—	—	—	—	—	—
+ 0.65 cc. TEL/gal.	—	—	100.0	—	—	—	—
+ 3.00 cc. TEL/gal.	—	89.0	—	97.5	97.5	98.0	100.0

Considerable discussion has centered around safety fuels for use in aircraft engines to reduce the fire hazard now present in conventional volatile-type fuels. Although the exact properties of an ideal safety fuel are not definitely known, such a fuel is generally considered to boil in the 150–205° range and to have a flash point above about 45°.

The U.O.P. selective polymerization process, used in the manufacture of isoöctane aircraft fuels, also produces material which can be fractionated to a product boiling in the safety-fuel range. The selective poly units are operated to produce maximum yields of isoöctenes. However, the reaction may also produce high yields of the heavier polymers which can be hydrogenated to safety aviation fuel. The properties of this type of fuel are given in Table 7. For comparative purposes data for isoöctane produced in the same operation have been included.

A safety aviation fuel can be obtained from the hydrogenated high-boiling fraction by distillation, which would yield a product of 98–99 octane rating if desired.

Table 7.

	Operation 1*		Operation 2*	
	Isooctane Fraction	High-boiling Material	Isooctane Fraction	High-boiling Material
Gravity (°A.P.I.)	66.4	50.5	68.5	58.1
100 cc. Distillation (A.S.T.M.)				
I.B.P. (°F.)	210	273	199	250
Per cent distilled over				
10	222	317	218	281
50	227	362	222	340
90	232	389	230	361
E.P. (°F.)	254	450	250	390
Octane No. (M.M.)	95	89	97	96
Reid Vapor Pressure (lbs.)	1.6	<0.5	1.7	<0.5

\* Charging Stock: Operation 1: one part isobutene to 1.2 parts *n*-butene. Operation 2: four parts isobutene to one part *n*-butene.

### Hot Sulfuric Acid Polymerization†

The Shell and Standard Oil Development Companies have a process for producing isooctane from the butenes present in cracked gases wherein sulfuric acid is employed as a catalyst at elevated temperatures. In this process both normal butene and isobutene react to form isooctene. An excess of normal butene is usually present. The process is shown in Fig. 8. In carrying out the operation of the process, the charge of butane-butene fraction and the acid reagent are introduced into the recycling line of the hydrocarbons undergoing treatment. Fresh acid is also added. The mixture of recycle stock, fresh acid and butane-butene fraction is discharged into a reactor cooler and then to a time reactor, in which the polymer is produced. The reaction is exothermic, and sufficient cooling is provided to maintain a temperature of about 80°. In present practice the acid concentration is about 70 per cent for a time of contact of 10 to 15 minutes. The mixture of hydrocarbons, polymer and acid, leaves the time reactor and flows into a separator where most of the acid is removed by gravity. The hydrocarbon and polymer stream leaving the separator is further cooled and passed into a final acid separator. The polymer is then debutanized.

The polymer product is mixed with caustic and heated with exhaust steam to neutralize acidic substances and to hydrolyze acid sulfates. After the removal of caustic soda, the product is passed to a second debutanizer, after which the dimers are separated from the heavier polymers and delivered to storage. The polymer product formed is stated to be about 90 to 95 per cent octenes, which upon hydrogenation have an octane value of about 95. The yield of octenes is said to be equal to twice the isobutene content of the feed stock when there is more normal butene than isobutene present in the original stock, which is usually the case.

### Catalytic Alkylation

One of the important commercial methods for the production of high-octane aviation fuel is the alkylation process employing sulfuric acid‡

†Process Handbook (1939), Gulf Publishing Co., Houston, Texas.

‡ See Paper 20th Annual Meeting of the American Petroleum Institute, Nov. 1939, by Anglo-Iranian, Humble Oil and Refining, Shell Development, and Texas Companies; also Morrell, U. S. Patent No. 2,169,809, Aug. 15, 1939, which covers the sulfuric alkylation process of converting isobutane and butenes to isooctanes.

as a catalyst. The reaction involved in this process is the direct addition of an olefin, for example, butene, to isobutane to form isoparaffins. This is readily accomplished by contacting the olefin with a large excess of the isoparaffin in the presence of a relatively large amount of sulfuric acid at an

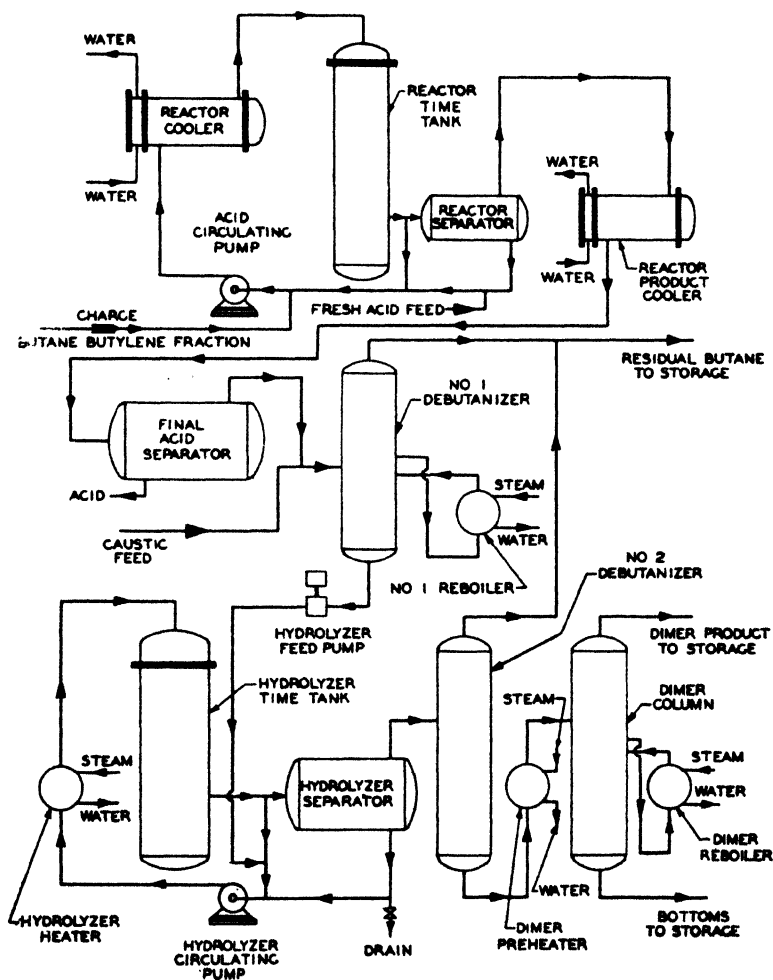


FIGURE 8.—Hot Acid Polymerization Process.

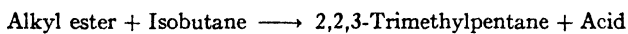
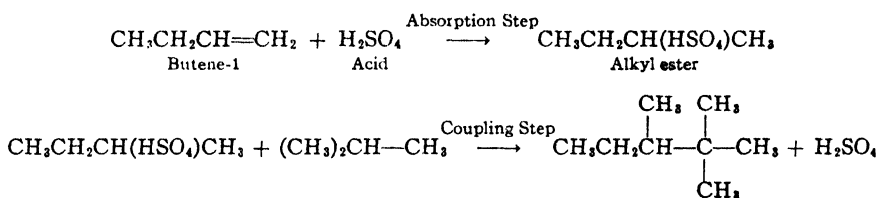
approximate temperature range between 0 and 30°, employing sulfuric acid concentrations of approximately 90 to 100 per cent.

Aviation fuels with octane ratings of 92–94, and in some cases higher, may be made by the use of this process; and, with the development of isomerizing processes to augment the volume of isobutane available by the

treatment of normal butane, the potential yields of isoöctanes by alkylation from the average refinery is greater than by the alternative method of making isoöctanes, namely, by the two-stage process of olefin polymerization, followed by hydrogenation. The alkylation process fits in well with many refinery operations, and the materials of construction and type of operation required are simple and in line with ordinary refinery operations.

Alkylation may also be readily carried out with the use of metallic halides, such as aluminum chloride and boron fluoride, but these processes have not as yet been developed to a commercial stage. The sulfuric acid process, however, owing to the cheapness of the catalyst and the possibilities of adapting the used sulfuric acid both to other refinery operations and to recovery, is excellent for practical adaptation.

The operation of a commercial process was presented in a paper at the 20th Annual Meeting of the American Petroleum Institute, Nov. 1939 (*loc. cit.*), and the reaction mechanism is described as follows:



To prevent the absorption step from proceeding to the point where the acid becomes useless, it has been found necessary to have a large excess of the isoparaffins.

In continuous operation the suppression of olefin absorption is brought about by first diluting the olefin feed with isoparaffins and then adding this mixture to an emulsion of acid and reacted hydrocarbon which is rich in isoparaffins and substantially olefin-free. In commercial plants mixing is performed by the use of a circulating pump and intimate contact is maintained by the velocity of flow through baffles or jets. A simplified flow diagram of a commercial plant submitted in the aforementioned article is shown in Fig. 9.

The acid is withdrawn at approximately 90 per cent concentration since there is a drop in acidity from approximately 98 to 90 per cent or lower, due to absorption of hydrocarbons in the reaction, although other reactions may be contributing factors.

The spent acid withdrawn is replaced by fresh acid, thus maintaining the efficiency of the operation. The quantity added is affected both by the composition of the feed stocks and by operating conditions. From one viewpoint, acid is not consumed but is diluted by the hydrocarbon, and a major part of the acid can be recovered by ordinary reconcentration methods, or it may be used for acid-treating various products of the refinery. Isobutane is the isoparaffin used in the process, since isopentane and isohexane are in themselves valuable components of gasoline. The charging stocks to be converted are preferably treated with a caustic wash

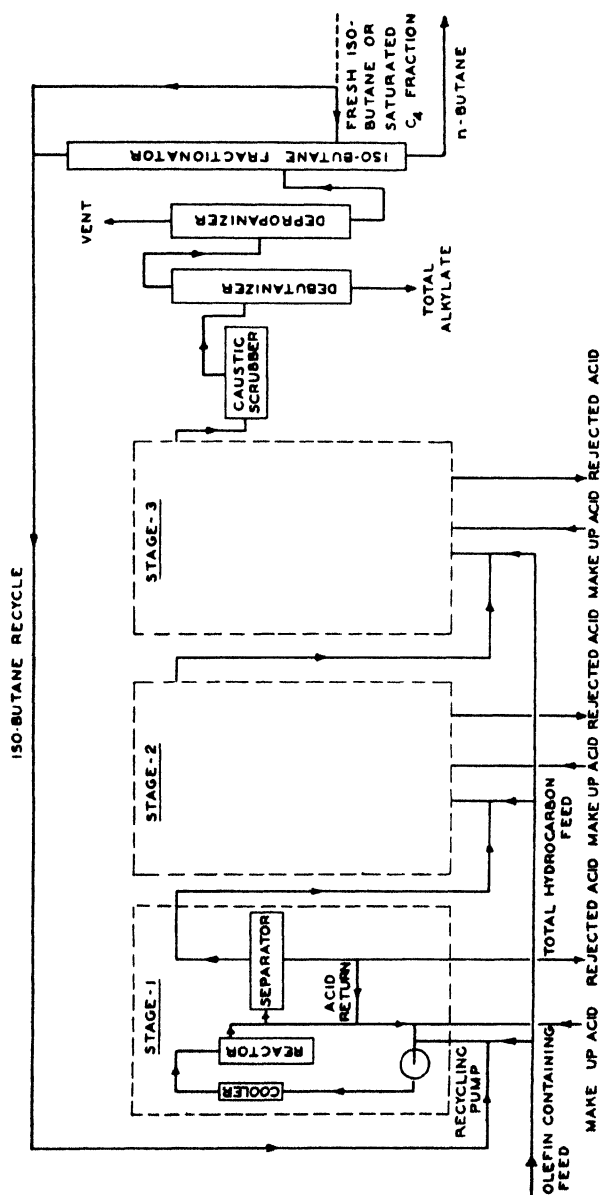


FIGURE 9.—Flow Diagram: Three-stage Sulfuric Acid Alkylation Plant, Split-olefin Feed.



to remove hydrogen sulfide and possibly other impurities. Amines may be removed by water washing.

The operating variables are isoparaffin-olefin ratio, contact time, acid strength, temperature, acid-hydrocarbon ratio, olefin concentration of the feed and degree of agitation. These variables are interdependent.

The isoparaffin-olefin ratio has a marked influence on the life of the acid and on the yield and quality of the product. The higher the ratio the better the results. Usually a 5:1 initial ratio is chosen as the preferred operation with isobutane and butenes. This ratio is, of course, very much higher in the mixture actually undergoing reaction. These high ratios are obtained by blending the olefin and the isobutane and by recycling the unreacted isobutane. Although the ratio of isobutane to olefin is high, the actual reaction of isobutane is theoretical. As pointed out previously, the isomerization process for the conversion of normal butane to isobutane will, no doubt, be a determining factor in the widespread use of this process.

The contact time is usually expressed by the ratio of the volume of hydrocarbons in the reaction zone to the volume of hydrocarbon feed per unit of time. Contact times of 5 to 50 minutes have been considered.

The make-up acid strength varies between 96 and 100 per cent. There is considerable difference between the actual strength in the reactor and the make-up acid due to the accumulation of hydrocarbons and some water, which may be present. The usual acid strength in the reactor has a titratable acid from 80 to 90 per cent, but this is different from the acid which is diluted with water to this extent owing to the character of the acid derivatives with which the acid is diluted. Therefore, the true acid strength may be somewhere between 90 and 98 per cent.

When temperatures much above 20° are employed, increasing oxidation of the hydrocarbons results. Therefore, lower temperatures favor increased catalyst life and better yields of the desired products. Temperatures between 0° and 10° have been found satisfactory. The volume of acid to hydrocarbon is usually about 1:1, but ratios as high as 2:1 have been used with good results.

Various types of mixing devices have been found satisfactory, *e.g.*, agitation by pump and recycling through a system of jets or baffles gives a simple and good method of carrying out the operation.

The products yielded by the alkylation process are highly suitable as aviation fuel because of their high octane number, high lead susceptibility, low sulfur content, and other desirable motor requirements. When isobutane and butenes are used, the product boils almost entirely in the gasoline boiling range with from 80 to 90 per cent below 150°. The product is free from gum and no substantial change occurs on prolonged exposure to sunlight and air.

This process has had remarkably rapid development, as there were 14 plants in operation or projected at the end of 1939 with a daily capacity of 13,000 barrels of aviation gasoline per day, and additional installations are being considered by many other companies.

### Catalytic Isomerization

Isomerization of hydrocarbons seems destined to receive wide and practical application in the petroleum and other industries, analogous to alkylation, aromatization, dehydrogenation, hydrogenation, and polymerization. Isomerization will be of great importance in the production of valuable selected hydrocarbons by reactions consisting only in a change of configuration, or rearrangement of carbon and hydrogen atoms. This reaction can be expected to become more efficient (requiring less expenditure of chemicals or energy) and to proceed with greater velocities as improved catalysts are developed.

One of the most important commercial aspects of isomerization is the conversion of normal butane into isobutane in connection with the production of isoöctane by direct alkylation of isobutane with butenes to produce isoöctane.

Direct isomerization of *n*-butane to isobutane takes place at 175° and 35 atmospheres' pressure in the presence of *anhydrous* aluminum chloride and *dry* hydrogen chloride. This reaction proceeds with a 13-per cent isobutane formation during a 4-hour reaction time.<sup>48</sup> A recent patent<sup>91</sup> discloses the conversion of butane into isobutane (66.5 per cent) by heating for 12 hours at 150° under 30 atmospheres' pressure in the presence of aluminum chloride (16.4 per cent) and hydrogen chloride (1.6 per cent).

Both normal and isobutane were isomerized in the liquid phase at about 30° and 3 atmospheres' pressure in the presence of aluminum bromide (18.9 per cent).<sup>60</sup> The isomerization proceeded rather slowly under these conditions, and over 2 months were required to reach equilibrium (78–82 per cent of iso and 18–22 per cent of normal), starting with either of the pure hydrocarbons. Traces of methane, ethane, and propane were formed as side products.

### Catalytic Cracking

One of the most important developments in catalysis as applied to the petroleum industry is the catalytic cracking process to improve the quality of gasoline produced from heavier oils. Yields of 85% of gasoline of 81 octane have been obtained from Midcontinent gas oil by the U.O.P. process.

This yield and quality of gasoline is based upon a recycle operation, but the extent of recycling is well within commercial practices on thermal cracking units. This yield also includes the yield from catalytic polymerizing of the cracked gases, 95 per cent of which may be polymerized as they leave the catalytic cracking plant. A typical cracked gas analysis follows:

H <sub>2</sub>	= 15.9%
CH <sub>4</sub>	= 18.5
C <sub>2</sub> H <sub>4</sub>	= 4.8
C <sub>2</sub> H <sub>6</sub>	= 5.2
C <sub>3</sub> H <sub>6</sub>	= 21.5
C <sub>3</sub> H <sub>8</sub>	= 5.1
iso-C <sub>4</sub> H <sub>8</sub>	= 8.8
<i>n</i> -C <sub>4</sub> H <sub>8</sub>	= 12.3
C <sub>4</sub> H <sub>10</sub>	= 5.0
O <sub>2</sub>	= 0.3
CO	= 0.6
N <sub>2</sub>	= 2.0

The balance of the yield is represented by 6 per cent residue oil of 25 gravity and about 9 per cent unpolymerizable gas and loss. The 85-per cent gasoline fraction contains monoolefins and is stable with respect to color and octane value and has about 10 pounds vapor pressure.

As an alternate operation the unit may be run to produce up to 5 per cent isoöctenes on a single-pass basis, or 12.5 per cent in a recycling opera-

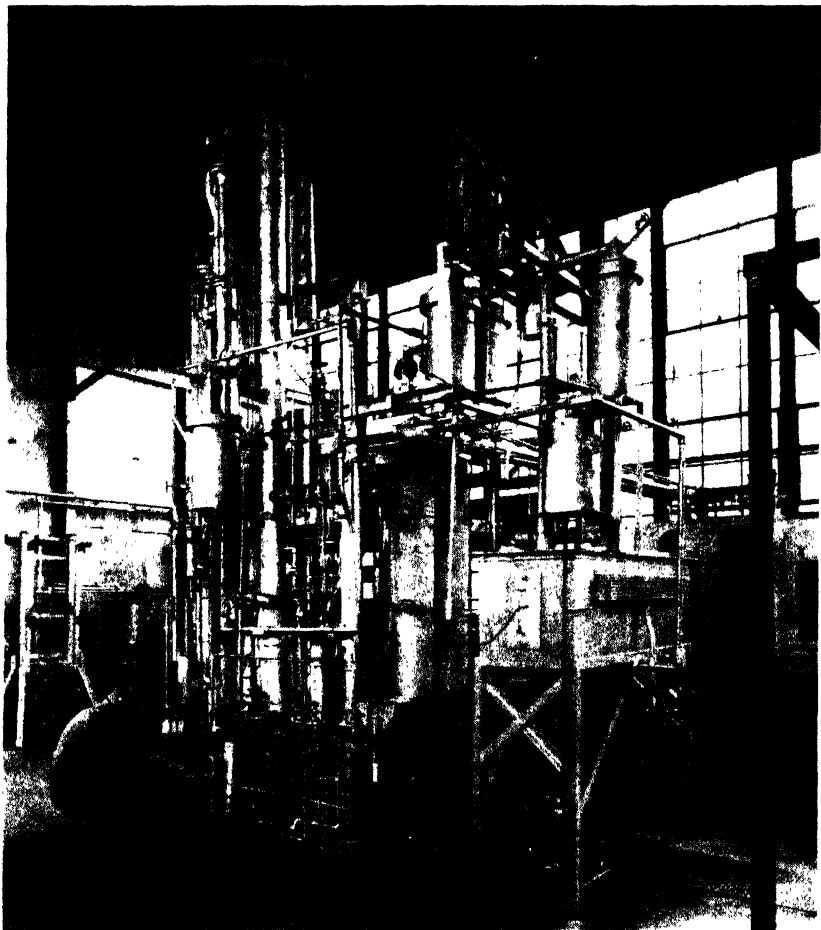


FIGURE 10.

tion. The isoöctene fraction may be hydrogenated to isoöctane gasoline. If the latter is recovered by hydrogenation of isoöctenes as an aviation gasoline, the balance of the motor fuel production of about 73 per cent by volume will be about 81 octane number.

The plant consists essentially of a heater, catalyst reactor, and automatic controls for alternating the flow of oil through the furnace and re-

actors, and another section is utilized for reactivating the catalyst. The cycle is about 40 minutes in duration.

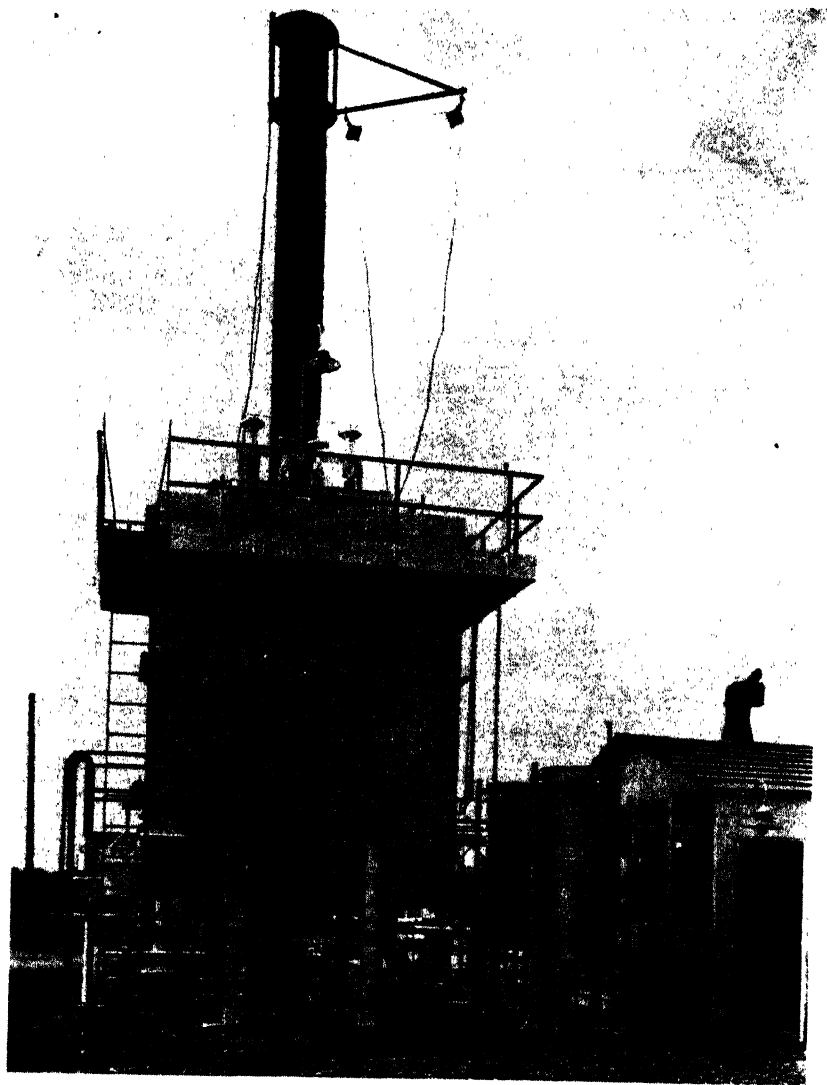


FIGURE 11.

The results mentioned above were obtained with gas oil, but it should not be understood that operation of the unit is limited to gas oils nor necessarily to overhead stocks. In fact, twenty types of charging oils have been investigated for the purpose of selecting the most practicable catalyst, and the range of stocks tested has extended from Kettleman Hills, California,

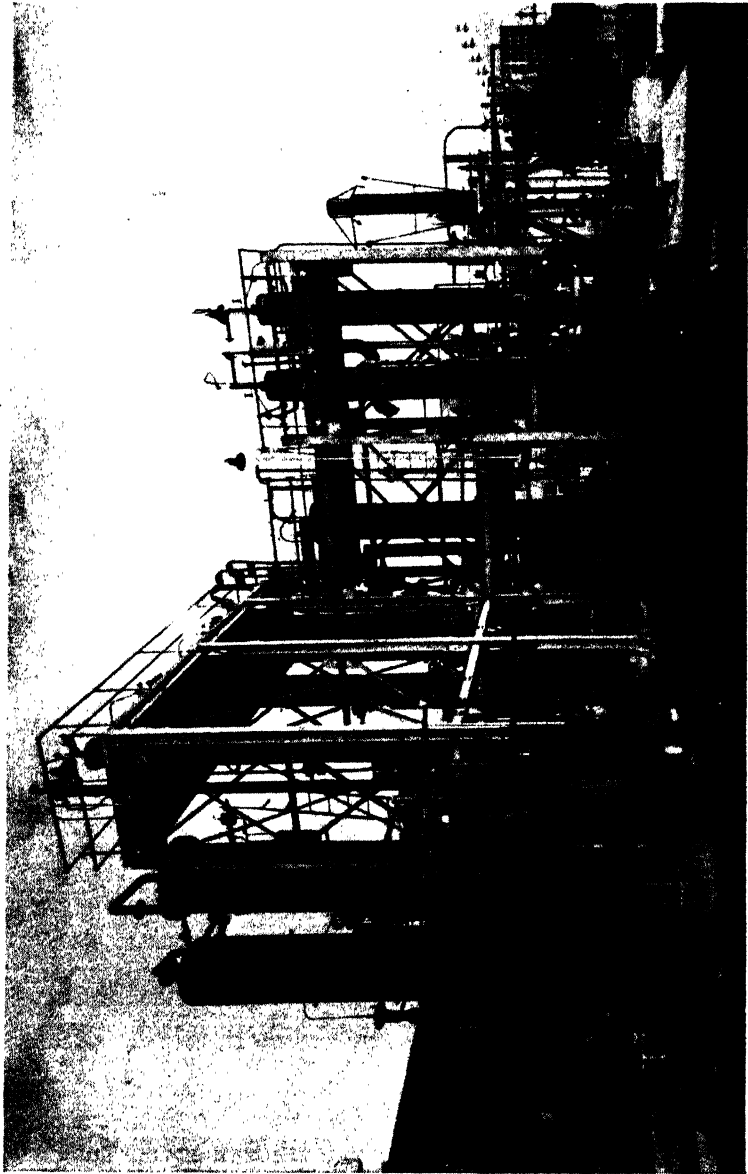


FIGURE 12.

residuum to Pennsylvania gas oil. Highly paraffinic overhead distillates are favored. By alternating the operating and regeneration cycles, long operating periods may be obtained.

Catalytic cracking units in laboratory and commercial development stages are shown in Figs. 10, 11 and 12.

The catalytic cracking unit may be described as banks of catalyst reactors, with automatic controls provided to alternate the flow of heated oil first through one-half of the catalyst reactors and then through the other, while the catalyst in the first reactors is being activated. In the unit shown, a pressure of 15 pounds is adequate to process the charge.

The catalyst used is of the alumina-silica type and appears to be exceptionally rugged. Revivification of the catalyst is accomplished by burning off the carbonaceous material which collects on the catalyst, and this in turn necessitates only passing a predetermined amount of air, or mixtures thereof with combustion gases, through the tube and maintaining a moderate temperature of combustion. The oxidation reaction progresses through the reactors under automatically controlled conditions. Prior to burning the carbon from the reactors, they are purged of oil vapors for a period of about 30 seconds.

Other types of catalytic cracking processes, such as those involving stationary beds and finely divided catalysts (the flow type of catalytic process), have been developed.

In the Houdry<sup>45, 92</sup> operation for the catalytic conversion of heavier oils into motor fuels, a 45-per cent yield of high-octane gasoline in one pass is obtained. The catalyst employed is stated to be an activated hydrosilicate of alumina. The operation employs two catalyst chambers used alternately for producing gasoline and regeneration, to permit continuous production. The flow diagram illustrates the process, Fig. 13, operating on crude oil with a single pass through the catalyst, the dotted line indicating the flow when it is desired to run on a "no residuum operation."

The oil is pumped through heat exchangers, where it is preheated with the product from the catalyst chambers, and then to a flash tower where the straight-run products are removed. The residue from the flash tower is pumped through a heater, where it is raised to approximately 470°, and from there into a vaporizer. The bottoms are removed as a liquid and the vaporized fraction of the charge is passed to the catalyst chambers. The vapors from the catalyst chambers are heat-exchanged with the crude oil and then passed into the final fractionating tower in which gasoline, furnace oil, and heavy gas oil are separated and withdrawn. The heavier oils may be recycled to the system. When distillates are used as charge, the flash tower and vaporizer may be eliminated. The yield of gasoline from this operation is about 45 per cent per pass, based on the charge to the catalyst, having an octane number of from 77 to 81, with blending values of from 4 to 10 points higher than the actual octane number. The catalyst has a long life and may be readily regenerated. A number of commercial units have been installed.

To show the probable reactions which take place in catalytic cracking



the following summary from "The Catalytic Cracking of Aliphatic Hydrocarbons," by Egloff, Morrell, Thomas and Bloch<sup>24</sup> is given:

"A number of hydrocarbons cracked at atmospheric pressure in the presence of an activated silica-alumina catalyst showed the following behavior:

"1. A mixture of *n*-butenes undergoes extensive catalytic isomerization to isobutene in the temperature range 200–315°C. accompanied by polymerization and cracking. Between 230° and 315°C. the isobutene content of the C<sub>4</sub>-product was  $24.1 \pm 1.5$  per cent.

"2. *n*-Pentenes showed reactions similar to those of the butenes, yielding 50 per cent of isopentenes at 205°C.

"3. A mixture of *n*-octenes undergoes both catalytic isomerization to isoöctenes and catalytic cracking to gaseous products consisting principally of equal amounts of normal and isobutene. The results are consistent with the theory that isomerization precedes cracking. In the temperature range 190–205° C., the conversion was over 80 per cent.

"4. The primary catalytic reaction of cetene in the range 150–230°C. was isomerization to isohexadecenes; the secondary reaction was cracking to lower-boiling olefins, accompanied by isomerization of normal olefinic products to iso-olefins. The isohexadecenes catalytically cracked approximately three times as rapidly as cetene itself.

"5. *n*-Octane catalytically cracked seven to eight times as rapidly as in thermal decomposition, and the catalytic products contained more C<sub>6</sub> and C<sub>7</sub> hydrocarbons and less methane, ethane, and ethylene than the pyrolytic reaction alone. The temperature required for the catalytic cracking of octane was 95°C. higher than that required for *n*-octenes.

"6. Cetane was catalytically cracked largely to C<sub>3</sub>, C<sub>4</sub> and C<sub>5</sub> hydrocarbons. The gasoline boiling range products contained both branched-chain and straight-chain hydrocarbons, in contrast to the products of cetene cracking, which were essentially all branched-chain.

"Although the behavior in thermal cracking of cetane and cetene is quite similar, cetane is far more stable toward catalytic cracking than cetene. In both cases, the products of catalytic cracking are quite different from those of pyrolytic cracking."

### Catalytic Reforming

The conversion of the lower-boiling distillates, such as gasoline and naphtha, into products of higher antiknock value is generally referred to as reforming. Gasolines and naphthas occurring in crude oil generally have to be reformed to increase their octane number, and this is accomplished by either thermal or catalytic treatment.

In the catalytic conversion of low-octane gasolines and naphthas, the charge is pumped through a heater after being heat-exchanged with the material leaving the heater. The oil undergoing conversion is heated to a temperature of 430–450°, the vapors leaving the heater passing directly to the catalyst chamber and from there through heat exchangers to a fractionating column, wherein they are separated into the desired fractions, which may include aviation gasoline, naphtha, and heavier oils.



During the conversion, carbon is deposited upon the catalyst; this is periodically burned off to regenerate the catalyst. The on-stream periods vary from ten minutes to an hour or longer, with regeneration periods of approximately one-half hour. The catalyst chambers are arranged so that while one is converting the other may be regenerating, and more than two catalyst chambers may also be employed if desired.

The catalysts may be in the form of granules or pellets when used in a stationary bed either in chambers or tubes, or they may be powdered and heated with the oil in a flowing stream. Catalysts of the silica-alumina and alumina-chromia types, as well as others, have been employed.

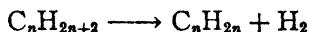
The arrangement of the catalytic reforming unit may be similar to the catalytic cracking unit. Eighty to ninety per cent of an 80-octane gasoline represents the range of product yield, depending upon whether the charge is predominantly paraffinic or naphthenic.

The octane value of the reformed gasoline is due not only to conversion of the paraffin hydrocarbons to aromatics, but also isomerization to isoparaffins. The product has an octane number of 80, high lead susceptibility, low gum, and in general may be made highly satisfactory for either motor or aviation gasoline.

### Catalytic Dehydrogenation

Frey and Huppke<sup>33</sup> found that the gaseous paraffins were dehydrogenated at atmospheric pressure in the presence of a chromic oxide gel at temperatures of from 350–500°. For example, in the case of *n*-butane at 500°, a yield of 14 per cent unsaturates was obtained, which were composed of 25 per cent 1-butene, 75 per cent 2-butene, and 1 per cent butadiene. The oxide gel catalyst loses its activity in the course of a few hours.

Grosse and Ipatieff<sup>36</sup> described some fundamentals of the catalytic dehydrogenation reaction for the conversion of paraffinic hydrocarbons to the corresponding olefins. It is based on the use of catalysts consisting of oxides of the transition metals of the 4th, 5th, and 6th groups of the periodic system on especially developed supports, such as alumina. Catalysts consisting of chromium oxide on alumina were found to be of particular importance. These catalysts have a long life, and are highly selective, and the conversion is in accordance with the general dehydrogenation equation:



The scission of the carbon-carbon bond, leading to the formation of carbon, methane, and other degradation products, is suppressed. Overall conversions of *n*-butane into *n*-butenes, isobutane into isobutene, propane into propene, and ethane into ethylene of 90 to 95 per cent of the theoretical are obtained. The process is also a source of practically pure hydrogen (more than 90-per cent). The latter is produced in amounts equal to the volume of olefin in accordance with the foregoing equation. The description of the chemistry and thermodynamics of the reaction, the identification of the reaction products, and the preparation of a laboratory catalyst are described by Grosse and Ipatieff.<sup>36</sup> The process usually operates at

pressures of around one atmosphere in the range of 500–750° (and at space velocities from 500 up to 10,000 or higher), depending upon the charging stock.

Burgin, Groll and Roberts,<sup>10</sup> of the Shell Development Company, described a dehydrogenation process using activated alumina as a catalyst,

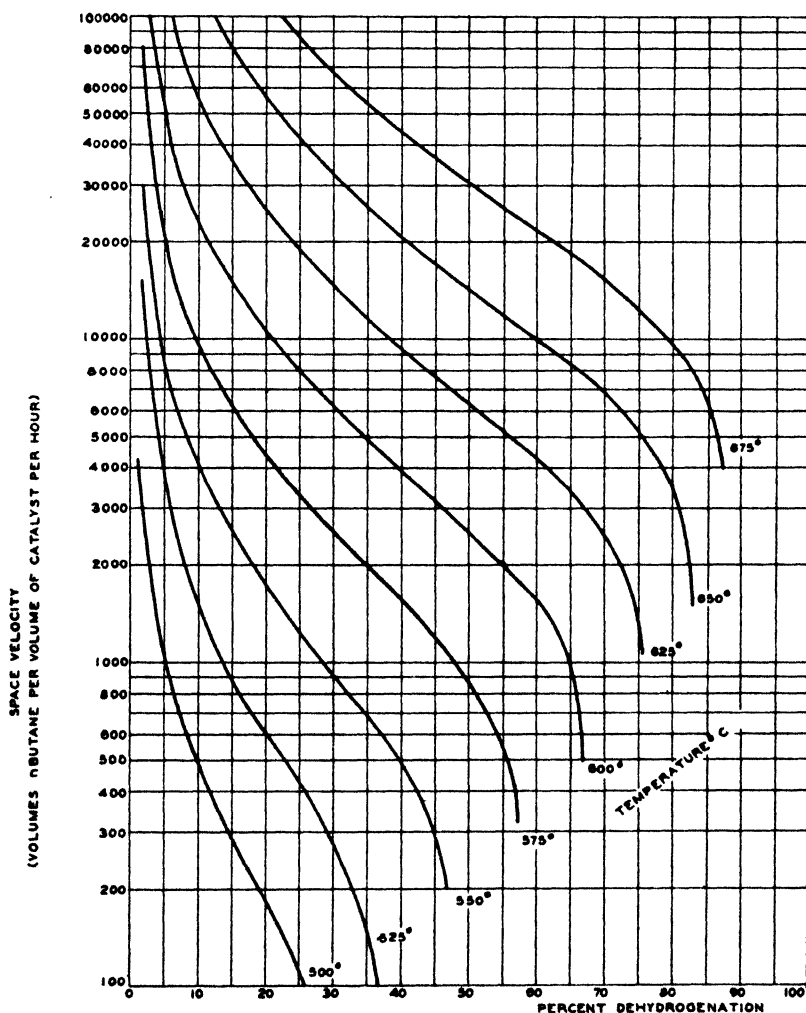


FIGURE 14.—Catalytic Dehydrogenation of *n*-Butane.

promoted by various metal compounds, particularly chromium oxide. A slight amount of water (referred to as a monomolecular layer) on the catalyst is stated to be necessary for the reaction; it does not occur in the absence of water. The Shell Development Co. have been pioneers in this work and in the field of dehydrogenation generally.

A description of the catalytic dehydrogenation process is contained in a

paper by Grosse, Ipatieff, Egloff and Morrell;<sup>38</sup> a summary of this description follows. Typical results with *n*-butane, illustrating the influence of temperature and space velocity on conversion, are shown in Figs. 14 and 15 as a comparison between the catalytic and the thermal treatment of *n*-butane. A chromium oxide catalyst on alumina was used.

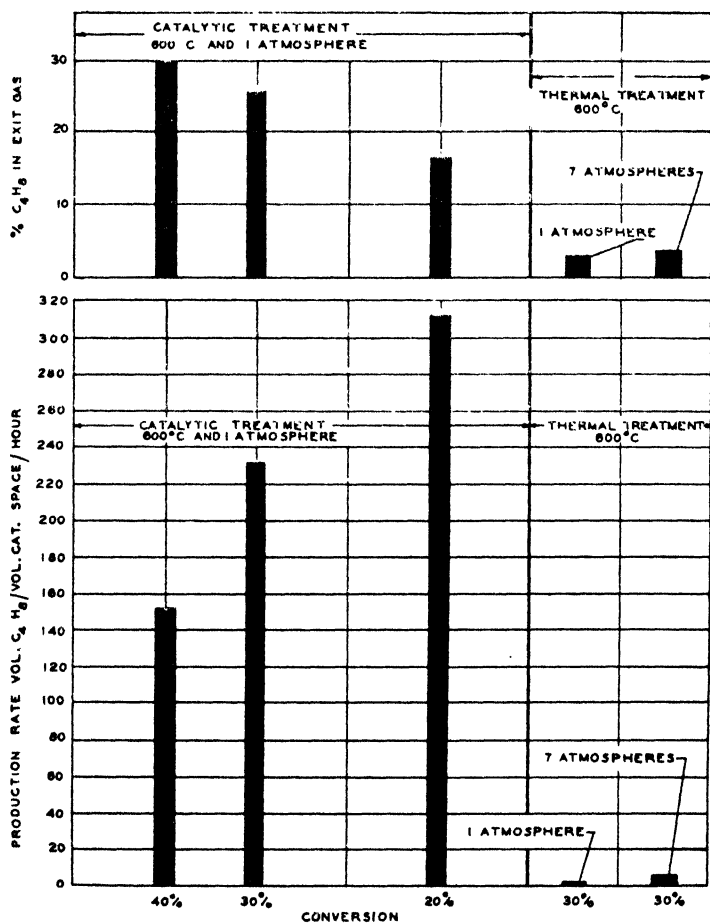


FIGURE 15.—Comparison of Catalytic and Thermal Treatment of *n*-Butane.

The process may be described best by reference to the flow chart, Fig. 16. The charging stock, which may consist of butanes or propane or a mixture thereof, for purposes of illustration here, consists essentially of a mixture of iso- and normal butanes.\* The butanes are passed through a heating coil in a furnace where they are heated to a temperature at which their substantial conversion into butenes will occur in the presence of a catalyst.

The heated butanes are passed from the furnace coil to one of a number

\* If desired, the *n*-butane, either partly or wholly, may be converted into isobutane by means of the catalytic isomerization reaction.

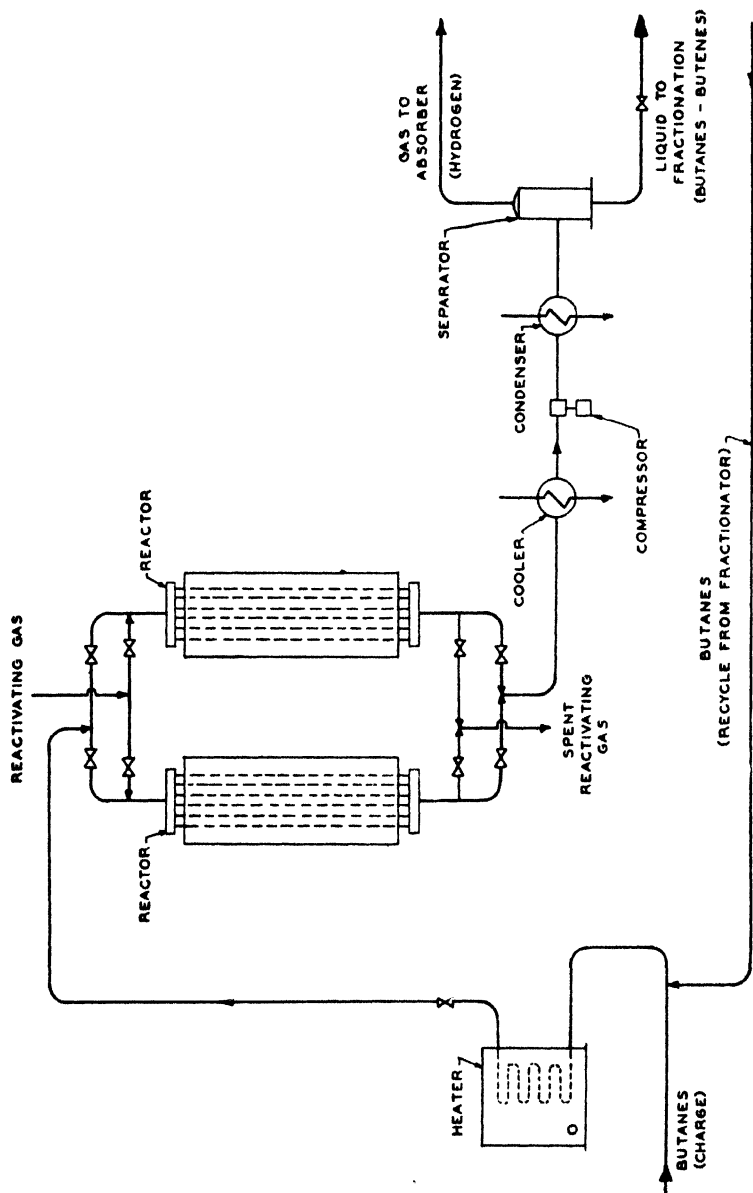


FIGURE 16.—Catalytic Dehydrogenation Process.

of reactors, each of which is alternately employed for conducting the dehydrogenating reaction and for reactivating the catalyst. The reactors are of the heat-exchanger type, having numerous tubular elements in which the catalyst is placed, and through which the reactants and resulting products are passed. A jacket is provided about the tubular elements, and a convective fluid may be circulated through the jackets of the reactors at a temperature regulated to control the temperature of the reaction taking place within the tubes. The material of the reactors must be such that the catalyst will not be poisoned by deposition of iron oxides. The catalyst is of the chromium oxide on alumina type. It is not poisoned by sulfur compounds or carbon monoxide.

During dehydrogenation in each reactor, carbonaceous materials are deposited on the catalyst, and progressively reduce its activity. To keep the catalyst in a sufficiently active state, the stream of heated butanes periodically and automatically is diverted from the reactor in which dehydrogenation has taken place and is supplied to another, similar reactor containing fresh or reactivated catalyst. It is a feature of this process that the length of the period or cycle is relatively short—of the order of one hour. Dehydrogenation of the butanes continues in the second reactor, while oxygen-containing gases are supplied in heated state to the reactor containing the fouled catalyst to burn the deposited carbonaceous materials from the catalyst mass and thereby effect its reactivation.

Spent reactivating gases and combustion products resulting from burning of the carbonaceous materials are discharged from the reactor in which reactivation of the catalyst is taking place, and are recycled for further use after their temperature and oxygen content have been readjusted to the desired value.

The products of catalytic dehydrogenation consist principally of iso- and normal butenes, unconverted butanes, hydrogen, and a small amount of methane, ethane and ethene, propane and propene. These products are continuously withdrawn from the reactor in which the dehydrogenating reaction is taking place through a suitable cooler to a compressor. After compression, the gases are cooled further and are passed to a separator from which a liquefied fraction, consisting essentially of butenes and unconverted butanes, and a gaseous fraction consisting essentially of hydrogen and the lighter hydrocarbon gases, are withdrawn separately. The gases from the separator are passed to an absorber in which their relatively heavy components, including any uncondensed butanes and butenes, are separated by absorption from a lighter gaseous fraction rich in hydrogen and suitable for use, when desired, to hydrogenate liquid products, such as isoöctene, resulting from polymerization of the butenes. The liquid fractions from the separator are supplied to suitable fractionating or stabilizing equipment in which they are substantially freed of undesirable dissolved light gases, and the resulting stabilized product may be sent to storage or directly to a catalytic-polymerizing process for conversion of the butenes into gasoline of high antiknock value. Unconverted butanes may be recycled back to the process.

Illustrations of the pilot or semi-commercial plant at Universal Oil Products Company's Riverside, Illinois, laboratories, which have a daily processing capacity of about 100,000 cubic feet of gas, are shown in Fig. 17.

The results obtained in typical operations are shown in Table 8.

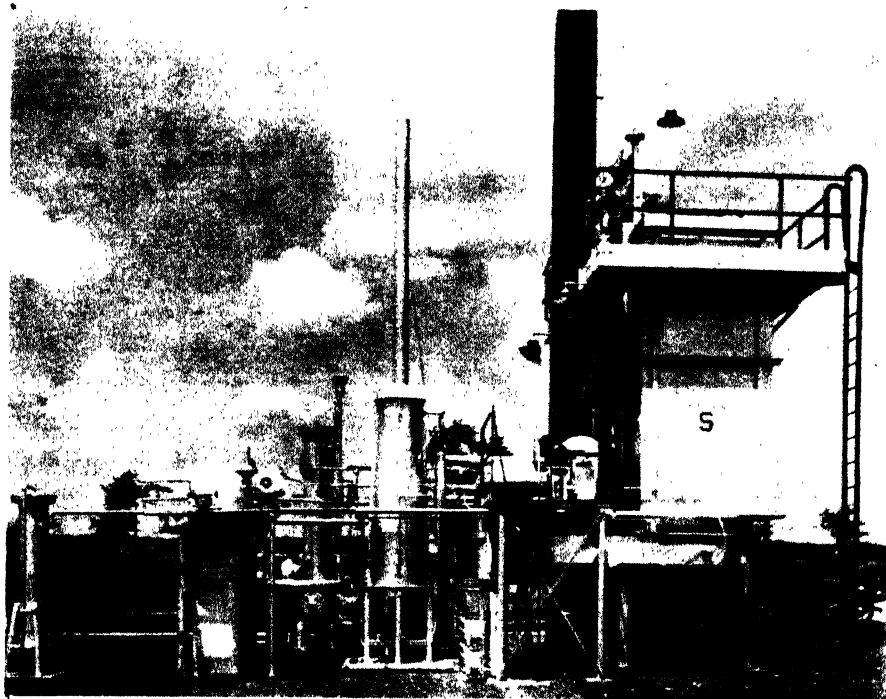


FIGURE 17.

### Catalytic Dehydrogenation-Polymerization-Hydrogenation

The dehydrogenation-polymerization-hydrogenation process for the production of isoöctane is illustrated by flow diagram, Fig. 18. This process is also applicable to the production of aviation fuel from mixtures of iso- and normal butanes.

The charging stock consists essentially of butanes. The proportion of isobutane to *n*-butane varies from 15 to more than 75 per cent. The octane rating of the hydrogenated polymer increases with the increase of isobutane in the charge.

The butanes are supplied at relatively low pressure to the preheater of the dehydrogenation unit, from which it emerges at approximately 580° and is directed to the dehydrogenation catalyst zone. The catalyst is of the chromium oxide on alumina type and is contained in vertical tubes externally heated by hot combustion gases. The butane passes through the catalyst at a high space velocity, and approximately 25 per cent of the charge is dehydrogenated. The gases leave the catalyst tubes at a pres-

Table 8.

	—Mainly <i>n</i> -Butane—			1 : 1 <i>n</i> - and <i>i</i> -Butane Mixture			—Mainly Isobutane—		
Periods on stream, from start	290-1	345-8	366-9	148-50	184-7	214-7	62-65	88-91	109-112
Space velocity, per hour.....	1,460	1,465	1,450	1,440	1,465	1,395	1,320	1,360	1,385
Average temp. of catalyst (°F.)	982	976	987	999	996	996	1,000	1,020	1,021
Inlet pressure (lb. per sq. in.)	52	52	52	52	51	52	60	62	69
Outlet pressure (lb. per sq. in.)	20	18	18	20	20	20	5	5	5
Inlet gas:									
Composition: Mole %									
C <sub>3</sub> H <sub>8</sub> .....	0.8	.....	1.0	2.7	3	3.5	4.6	8.8	9.4
<i>i</i> -C <sub>4</sub> H <sub>10</sub> .....	13.1	16.8	16.7	58.8	40	42.0	77.1	78.7	79.0
<i>n</i> -C <sub>4</sub> H <sub>10</sub> .....	86.1	82.3	82.3	37.2	56	54.2	18.3	12.5	11.6
C <sub>3</sub> H <sub>12</sub> .....	.....	0.9	.....	1-3	1	0.3	.....	.....	.....
Outlet gas:									
Composition: Mole %									
H <sub>2</sub> .....	17.3	18.0	18.1	21.2	18.8	20.2	18.4	21.6	20.1
CH <sub>4</sub> .....	1.4	1.6	1.7	1.9	1.8	3.2	1.8	2.0	1.2
C <sub>2</sub> H <sub>4</sub> and C <sub>2</sub> H <sub>6</sub> .....	0.5	0.5	0.19	0.2	0.1	0.5	.....	.....	0.7
C <sub>3</sub> H <sub>6</sub> .....	0.4	0.3	0.9	1.0	1.0	0.8	1.2	1.8	1.6
C <sub>3</sub> H <sub>8</sub> .....	1.5	1.3	1.5	4.4	5.2	3.4	4.4	7.4	8.1
<i>i</i> -C <sub>4</sub> H <sub>10</sub> .....	3.3	2.9	3.2	10.9	7.0	6.9	13.3	12.7	11.6
<i>n</i> -C <sub>4</sub> H <sub>10</sub> .....	15.9	15.7	17.0	9.9	12.2	12.1	3.4	5.9	5.5
C <sub>4</sub> H <sub>10</sub> .....	59.7	59.7	56.7	50.4	53.3	52.7	57.5	48.6	51.2
Conversion:									
Moles C <sub>4</sub> H <sub>8</sub> converted per 100 moles C <sub>4</sub> H <sub>10</sub> charged.....	25.7	24.9	28.1	31.6	29.5	29.0	24.9	30.8	28.1
Conversion corrected to 1,050° F. and 2,000 space velocity per hour.....	36	36	37	38	37	36	31*	33*	30*
Efficiency (mole C <sub>4</sub> H <sub>8</sub> per 100 moles C <sub>4</sub> H <sub>10</sub> converted).....	93	94	91	89	86	88	88	86	86
Yield per pass (mole C <sub>4</sub> H <sub>8</sub> per 100 moles C <sub>4</sub> H <sub>10</sub> charged).....	24	23	26	28.2	25.4	25.6	21.8	26.5	24.0
Yield per pass corrected to 1,050° F. and 2,000 space velocity per hour.....	33	34	34	34	32	32	27	28	26

\* Lower conversions partly due to high propane content of charge.

sure only slightly above atmospheric and at a temperature of approximately 610°.

The butane-butene mixture and hydrogen from the dehydrogenation system are cooled and compressed to approximately 100 to 200 pounds per square inch and then are passed to an adsorber, where the hydrogen is separated. A stripper is provided for removing the butane-butene mixture from the absorption oil, which is cooled and returned to the absorber.

The butane-butene product is pumped at high pressure to the polymerization unit of the process employing the solid U.O.P. phosphoric acid catalyst. The temperature employed here is 120-180° and the pressure 750 to 1,500 pounds per square inch. The temperature is controlled by a water-jacketing system around the reactor tubes. At higher temperatures a greater proportion of the normal butenes is polymerized, but a hydrogenated product of lower octane number is produced. The temperature, therefore, is determined by the octane number of the product desired. Steam produced from the reactor jackets, because of the exothermicity of the reaction, is used to preheat the feed. The polymer is debutanized, distilled, and catalytically hydrogenated to end-point aviation gasoline of approximately 97 octane number.

Only about 10 per cent bottoms (heavy polymers such as trimers) are recovered as a residue. The unreacted normal butenes from the debutanizer are led to a secondary polymerization stage, generally operated at higher temperature (*i.e.*, 250°) than in the selective polymerization sec-

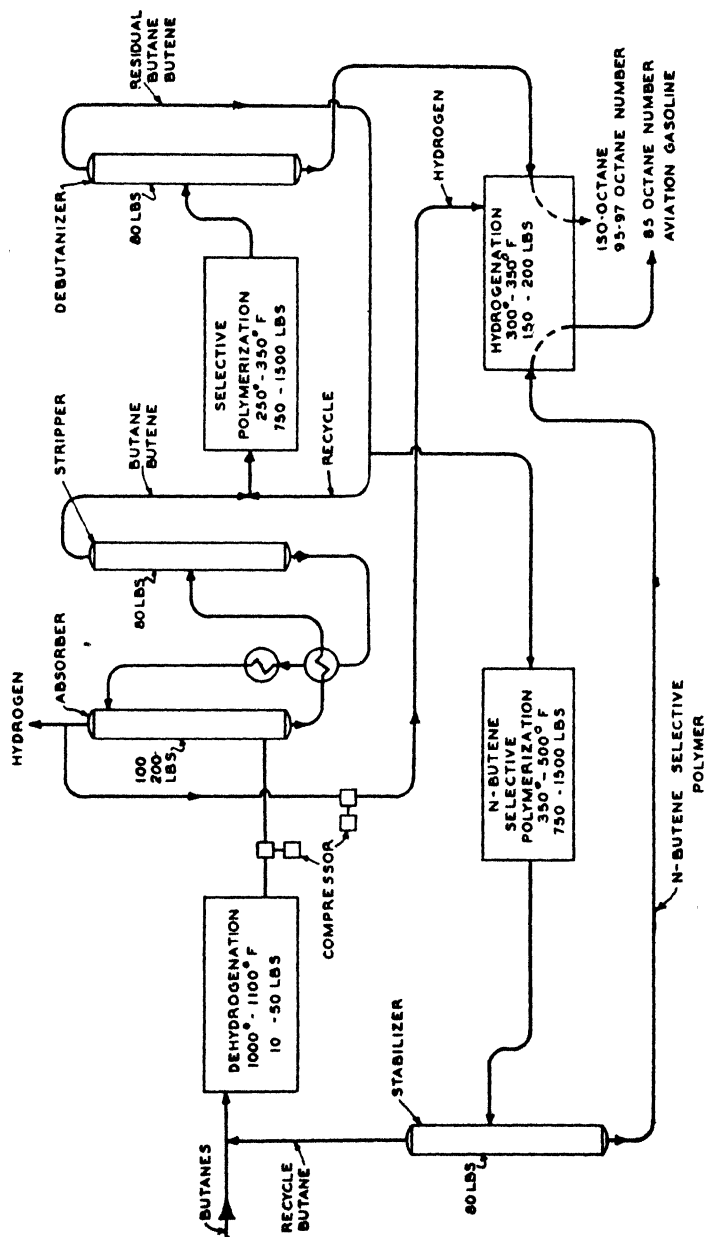


FIGURE 18.—Isooctane Process via Dehydrogenation-Polymerization-Hydrogenation.



tion. Temperature control is similar to that in the selective polymerization operation. The polymer product of the butene-selective polymerizing step passes through the stabilizer where the liquid polymers are separated from the butanes. The butanes are returned to the dehydrogenating step of the process. The polymer, when rerun and hydrogenated, yields a product of approximately 85 octane number.

The hydrogenation unit is operated alternately on the selective polymer and the residual butene polymer. A nickel catalyst is employed for hydrogenation. The hydrogen produced by dehydrogenation of the butanes is twice that required for hydrogenation of the polymer products. The rerun polymer and the hydrogen gas are supplied at a pressure of 150 to 200 pounds per square inch to the hydrogenation reactor tubes. As the nickel catalyst is sensitive to sulfur compounds, it is preferable to desulfurize the butane before dehydrogenation. If not desulfurized, the material first is passed through a guard reactor, which is filled with spent hydrogenation catalyst for removing sulfur compound impurities, and then is passed through two reactors in series, being hydrogenated by the gas in concurrent flow. As hydrogenation is also an exothermic reaction, essentially the same method of temperature control as in polymerization is used. The temperature is maintained at approximately 180°, and the outlet pressure at about 35 pounds per square inch, or just sufficient to depress the vaporization of excessive amounts of iso-octane in the spent gas. The hydrogenated product from the selective polymerization step consists essentially of iso-octanes.

For comparison, an operation is described by Egloff, Morrell and Nelson<sup>20</sup> wherein butanes and propane are pyrolytically cracked to produce olefin hydrocarbons, followed by catalytic polymerization to produce polymer gasoline.

### Gas Cracking and Catalytic Polymerization

A combination gas cracking and catalytic polymerization unit for the conversion of butanes and the polymerization of the olefins produced is in commercial operation, processing 1,090 barrels of butane a day. The butane cracking at high temperature and pressure produces relatively small amounts of pyrolytic gasoline. The cracked gases are polymerized catalytically as already described.

Referring to Figs. 19 and 20, butanes from the charge tank are pumped through a heater which operates at a pressure of about 750 pounds and a transfer temperature of 575–580°. Sufficient soaking time is provided in the heater to produce the desired conversion of about 50 per cent of the charge. The transfer material is cooled to about 30° under full plant pressure, and is released into the demethanizer column which operates at 300 pound pressure. In this column substantially all the methane and part of the ethane and ethylene are removed overhead, and the remaining components are removed as bottom product. This separation is accomplished by using debutanized pyrolytic polymer as absorption oil in the pot of the column and partially stripping the liquid in the bottom of the column through reboiling.

The bottom product from the demethanizer is discharged into the

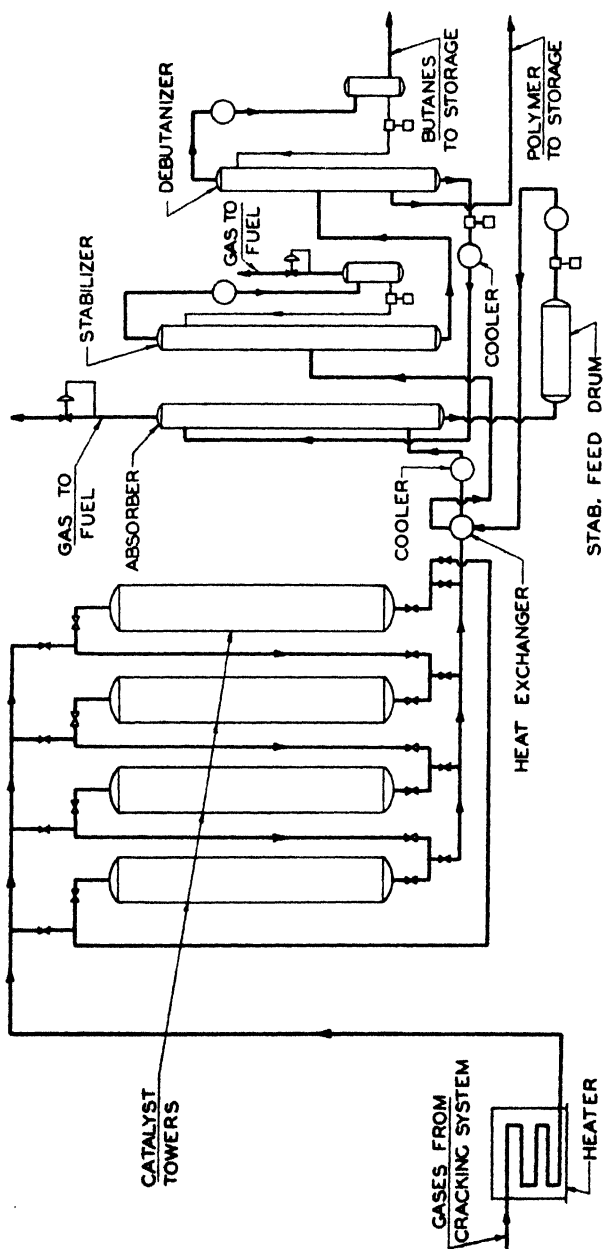


FIGURE 19.—Flow Diagram of Catalytic Polymerization Unit.

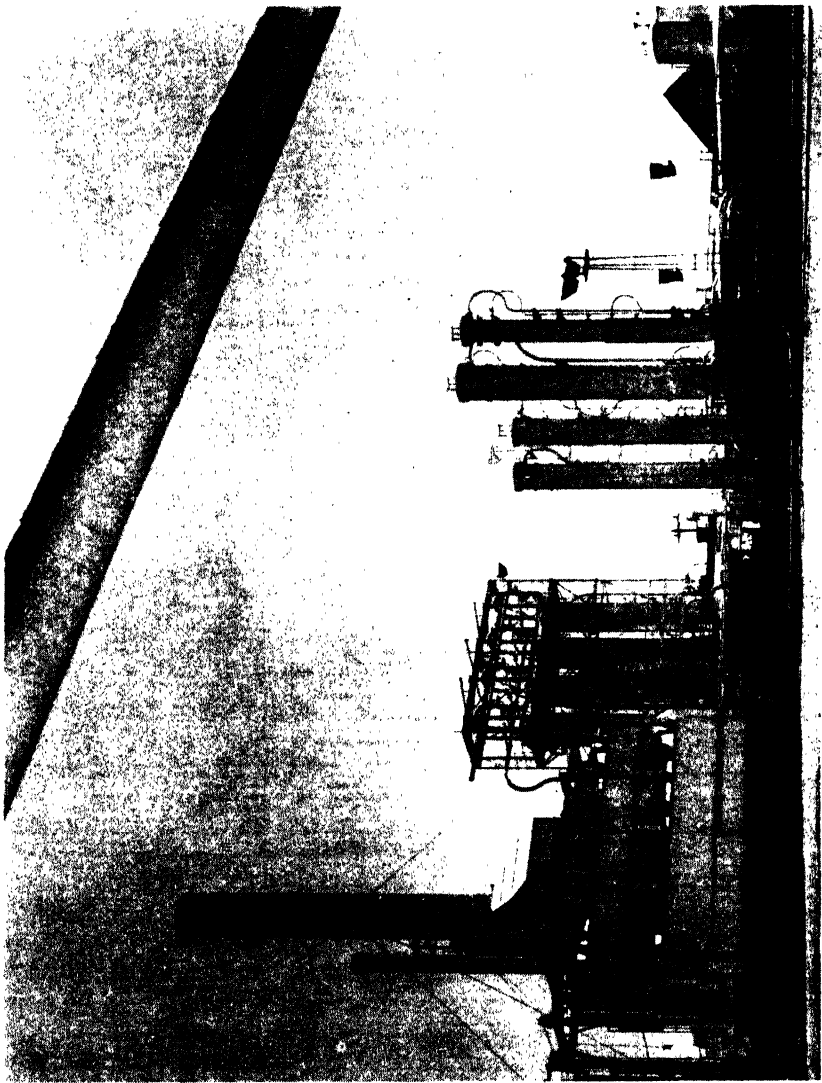


FIGURE 20.

debutanizer column. This column is operated at sufficiently high pressure so that the overhead gases may be satisfactorily processed in a catalytic-polymerization plant. These overhead gases, which include all of the butane-butenes and lighter hydrocarbons produced during the cracking reaction, with the exception of those discarded from the demethanizer column, contain from 25 to 28 per cent of propene-butenes. A debutanized pyrolytic polymer is removed from the bottom of the column. Part is recirculated to the demethanizer column as absorption oil, and the remainder passes to storage.

The polymerization unit is of the same type already described. It is followed by conventional fractionation equipment for the separation of catalytic polymer of the desired vapor pressure, and residual butane. It has been found advantageous to remove hydrogen sulfide from the butane before charging to the unit, since this results in the production of doctor-sweet products.

In a typical operation, the butane fraction from the natural gasoline plant used as a charging stock for the cracking-catalytic polymerization unit showed the analysis given in Table 9.

Table 9. Analysis of Butane Fraction.

	Mol %
Propane	3.3
<i>n</i> -Butane	83.2
Isobutane	12.2
Pentane	1.3

At the rate of 1,090 barrels per day, this charging stock was heated to a temperature of 575° and 750 pounds pressure in the cracking unit, from which 109 barrels per day of pyrolytic polymer gasoline of 4.7 Reid vapor pressure was produced, having additional properties as shown in Table 10.

Table 10. Pyrolytic Polymer Gasoline.

Gravity (°A.P.I.)	48.5
100 cc. Distillation (A.S.T.M.)	
I.B.P. (°F.)	119
Per cent distilled over	
10	147
20	159
50	202
90	407
E.P. (°F.)	520
Octane No. (C.F.R. Method)	74
Reid Vapor Pressure (lbs.)	4.7
Sulfur (%)	0.22

The hydrocarbon gases from the debutanizer of the butane cracking unit were analyzed for their propene and butene content which showed 27.7 per cent. This gas was passed through the catalytic polymer gasoline unit, producing at the rate of 293 barrels per day based upon the original 1,090 barrels of butane processed. The analysis of the polymer gasoline produced is shown in Table 11.

The approximate volumes of hydrocarbon gases available in the United States in 1939 are given in Tables 12 and 13.

Table 11. Catalytic Polymer Gasoline.

Gravity (°A.P.I.)	67.9
100 cc. Distillation (A.S.T.M.)	
I.B.P. (°F.)	95
Per cent distilled over	
10	134
20	157
50	209
90	333
E.P. (°F.)	430
Octane No. (C.F.R. Method)	81
Reid Vapor Pressure (lbs.)	8.3
Sulfur (%)	0.01
Gum (A.S.T.M.) (mg.)	12.3
Gum (copper dish) (mg. per 100 cc.)	81

Table 12. Hydrocarbon Gases Produced in the United States in 1939.

(Billions of Cubic Feet)

	Natural Gas	Refinery Gas Crude Distillation	Cracked Gas	Total
Cubic feet	2,500	250	350	3,100
	%	%	%	
Methane	69	61	53	
Ethane	14	21	15	
Propane	9	12	5	
Butanes	5	4	2	
Ethene	—	—	6	
Propene	—	—	13	
Butenes	—	—	6	

Table 13. Hydrocarbon Gases in 1939.

(Billions of Cubic Feet)

	Natural Gas	Refinery Gas Crude Distillation	Cracked Gas	Total Hydrocarbon Gas (Cubic Feet)
Methane	1,725	152.5	185.5	2,063.0
Ethane	350	52.5	52.5	455.0
Propane	225	30.0	17.5	272.5
Butanes	125	10.0	7.0	142.0
Ethene	—	—	21.0	21.0
Propene	—	—	45.5	45.5
Butenes	—	—	21.0	21.0

The yearly volumes of ethene, propene, and butenes, potentially available in the United States, are shown in Table 14.

Table 14. Ethene, Propene, and Butenes Potentially Available by Catalytic Dehydrogenation and Cracked Gases.

(Billions of Cubic Feet Annually)

Ethene	420.5
Propene	290.5
Butenes	148.8

The potential polymer gasoline of 81 octane number available from ethene, propene, and the butenes—on the assumption that it is all used for this purpose—is at the yearly rate of 8,345,000,000 gallons. The break-up of this volume of potential polymer gasoline is shown in Table 15 and is

based on only 25 per cent of the ethene polymerizing with the propene and butenes, which is the actual commercial performance when using the catalytic process of polymerization.

Table 15.

	81-Octane Polymer Gasoline (Gallons)
Ethene	420,000,000
Propene	4,650,000,000
Butenes	3,275,000,000
Total	8,345,000,000

The polymer gasoline of 80-octane number from butenes may be used as motor fuel or blended with low-grade gasoline to increase its octane rating. When aviation gasoline is the desired product, the butenes present in cracked or dehydrogenated gases are selectively polymerized so as to produce isoöctenes by the reaction of normal butene and isobutene in the ratio of 1:1, which in turn is converted into isoöctanes of 96-octane number. The volume of 96-octane aviation gasoline potentially available from the butenes is more than 2,180,000,000 gallons a year. The normal butene left over in the residue gas from the first polymerization reaction is subjected to polymerization in a second step which, upon hydrogenation, produces a saturated 85-octane aviation gasoline stock. The annual volume of this product potentially available is 1,095,000,000 gallons.

The potential aviation and polymer gasolines from the volumes of starting gases given in Table 15 are shown in Table 16.

Table 16. Aviation and Motor Gasoline.

	80-Octane Polymer Gasoline	85-Octane Aviation Base	96-Octane Aviation Base
Ethene	420,000,000	—	—
Propene	4,650,000,000	—	—
Butenes	—	1,095,000,000	2,180,000,000

Many economic situations exist in which it is more desirable to alkylate isobutane with ethene, propene, or butenes than to use the combination processes of polymerization and hydrogenation. It is estimated, as an average, that normal and isobutane are present in the ratio of 75 to 25 per cent. This means that there is potentially available about 35,500,000,000 cubic feet of isobutane in the gases listed in Table 17.

Table 17. Aviation Gasoline Potentially Available from Hydrocarbon Gases.

Process	Gallons	Octane No.
Dehydrogenation	2,180,000,000	96
Polymerization		
Hydrogenation (from butanes-butenes-hydrogen)	1,095,000,000	85
Total	3,275,000,000	92 Ave.
Thermal Alkylation:		
Neohexane	1,290,000,000	95
Isobutane and ethylene		
Sulfuric Acid Alkylation:		
Isobutane and butenes	1,715,000,000	93

Thermal alkylation—combining isobutane with ethene at high temperature and pressure, producing neohexane of 95 octane rating—has a yearly potential production of 1,290,000,000 gallons, on the assumption that all the isobutane available is used in this process.

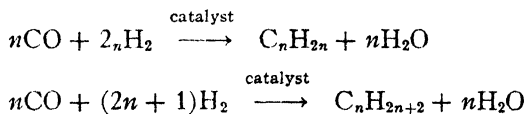
The catalytic sulfuric acid alkylation process may use propene and butenes with isobutane to form alkylate. The volume of alkylate from propene and isobutane potentially available, if all the isobutane were used, would be 1,500,000,000 gallons of 85 octane rating. If butenes are used for alkylation with isobutane, the yearly volume available of alkymer would be 1,715,000,000 gallons of 93 octane rating.

#### SYNTHETIC MOTOR FUELS FROM COAL

##### Hydrogenation of Carbon Monoxide, Coal and Oil

The Fischer-Tropsch process is applied in the production of synthetic petroleum by passing a mixture of carbon monoxide and hydrogen, *i.e.*, water gas, produced by treating coke or coal with steam, over a catalyst at pressures from atmospheric to about 15 atmospheres and at temperatures of 200–275°. A yield of approximately 50 per cent hydrocarbons, ranging from methane to solid paraffin wax, has been obtained by this process. Iron or cobalt catalysts, mixed with zinc or chromium oxides, or the oxides of the rare earths, were found to be satisfactory. Simple cobalt, nickel and iron catalysts have been used with good results. By increasing the pressure and using a somewhat different catalyst, for example, iron containing various alkalis, a mixture consisting of alcohols, ketones and aldehydes resulted.

The reaction may be represented generally as follows:



This process is in commercial operation in Germany where it is necessary to produce synthetic petroleum to supply part of the motor fuel needs.

In the operation of the process, water gas generated from coke and somewhat enriched in hydrogen so as to contain two parts of hydrogen to one of carbon monoxide by volume, or coke oven gas, the composition of which is altered to suit the requirements, is treated to remove sulfur, and is then passed at atmospheric pressure over a catalyst of nickel-thorium, cobalt-thorium and nickel-aluminum-manganese or, preferably, cobalt on a carrier, such as kieselguhr, at a temperature varying between 200° and 275°. Seventy-two per cent of the theoretical yield of 1.4 gallons of synthetic oil per 1,000 cubic feet of synthetic gas has been obtained, *e.g.*, the theoretical yield of hydrocarbons from one cubic meter of gas ( $2\text{H}_2 + \text{CO}$ ) is 208 grams, and yields of 140 grams have been reached commercially in a one-stage operation.

Table 1<sup>90</sup> shows the yields of hydrocarbons as a function of pressure employing a cobalt catalyst.

Table 1. Yields of Hydrocarbons at Different Pressures.

Gauge Pressure (atm.)	Yield, <sup>a</sup> Grams per Cubic Meter <sup>b</sup>				
	Solid and Liquid Hydrocarbons	Paraffin Wax	Oil (Above 200°)	Gasoline Fraction (Below 200°)	Gaseous Hydrocarbons, Including C <sub>3</sub> and C <sub>4</sub>
0	117	10	38	69	38
1.5	131	15	43	73	50
5	150	60	51	39	33
15	145	70	36	39	33
50	138	54	37	47	21
150	104	27	34	43	31

<sup>a</sup> Average yields per cubic meter of ideal gas over 4 weeks' operation with a single passage of the gas over the catalyst and without revivification of the catalyst.

<sup>b</sup> Under normal conditions.

The data in Table 1 indicate that at pressures of 5 to 15 atmospheres the formation of heavier hydrocarbons predominates over that of the lighter hydrocarbons, including the tendency to produce more wax. The activity of the catalyst is decreased to some extent by the accumulation of wax on its surface, but in general the pressure operation apparently increases the life of the catalyst.

Yields reported by others show: C<sub>3</sub> and C<sub>4</sub> fractions, 8 per cent; Kogasin I (gasoline boiling up to 200°), 62 per cent; Kogasin II (a mixture of naphtha, Diesel oil, and solid paraffin wax), approximately 30 per cent. The Diesel oil from the heavier oil fraction amounts to about 24 per cent of the total product and the wax about 21 per cent. The total gasoline from the first and second fractions is approximately 34.5 per cent.

The octane rating of the gasoline is quite low (40 octane) and as is usual, increases with the lower-boiling fractions. Reforming and adding tetraethyl lead to the gasoline will bring it up to a satisfactory motor gasoline. The Diesel oil on the other hand, as would be expected, due to its high paraffinicity, has a high cetane value, so that the process is eminently suited to produce this product. The paraffin wax and naphthenes have been found quite useful for the production of synthetic fatty acids by oxidation and subsequent conversion into soaps. The conversion of the olefin components of the lower-boiling fractions into lubricating oils by polymerization employing aluminum chloride has also been established. Fig. 21 shows a diagrammatic flow of the Fischer-Tropsch process for the production of motor fuel from coal carbonization and the catalytic water gas reaction.

The industrial process consists of the production of synthesis gas with a hydrogen-to-carbon monoxide ratio of 2:1, purification of the gas, synthesis of the hydrocarbons (including manufacturing and reclaiming of the catalyst), recovery of the hydrocarbons, and treatment of the same. The reaction is exothermic and is controlled by water-cooling to form steam. Direct cooling by oil, water, or gas has also been considered. Ordinarily, a tubular catalyst chamber is employed, the catalyst being placed outside of the tubes and water circulated inside. Sometimes this procedure is reversed. The catalyst life is approximately four to six months, after which the catalyst components may be regenerated and used for the preparation of fresh catalyst.

There are many approaches for the improvement of the product. For example, Egloff, Morrell and Nelson<sup>20</sup> obtained a yield of 84 per cent by



volume of 66-octane gasoline by thermal cracking of the product, which included polymerization of the cracked gases. In the light of more recent developments, various catalytic processes may be applied to the treatment of both the liquid and gaseous products to improve the octane values.

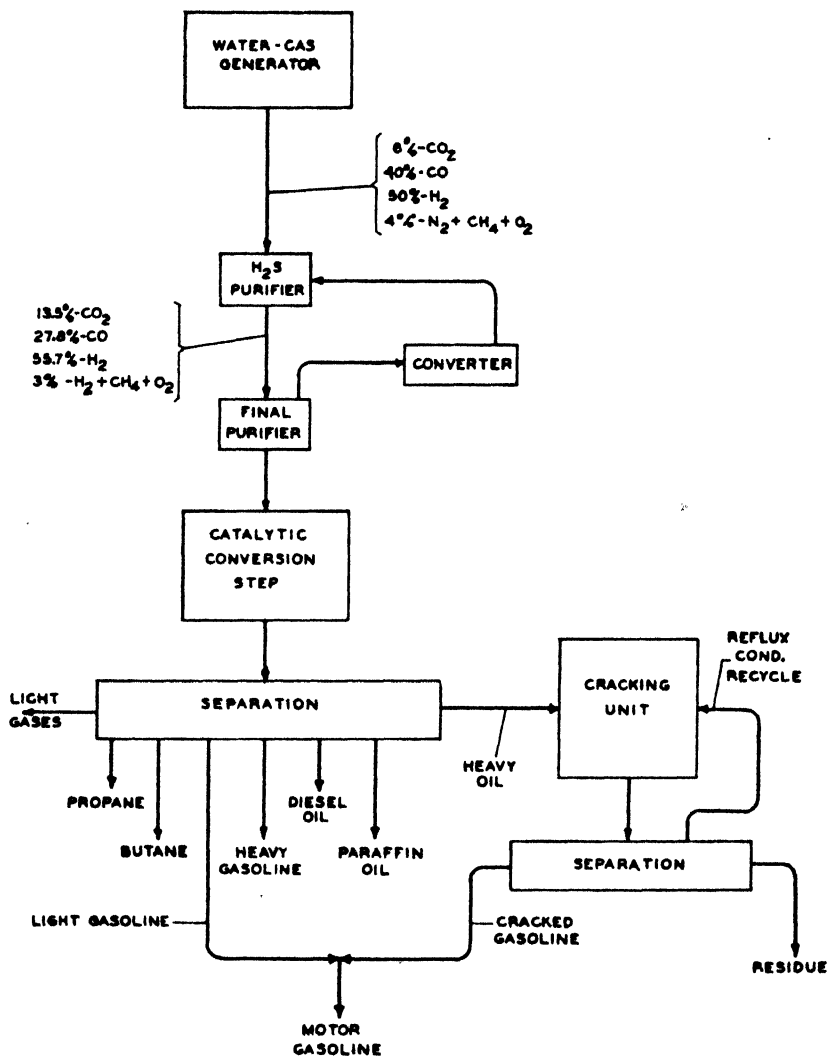


FIGURE 21.—Motor Fuel from Water-gas Reaction; Tischer-Tropsch Process plus Cracking.

The first Tischer-Tropsch industrial plant went into operation in Germany in 1936, and at the present time (1940) over 1,000,000 tons of liquid product are being produced annually in Germany by this process. Plants have also been built in other countries.

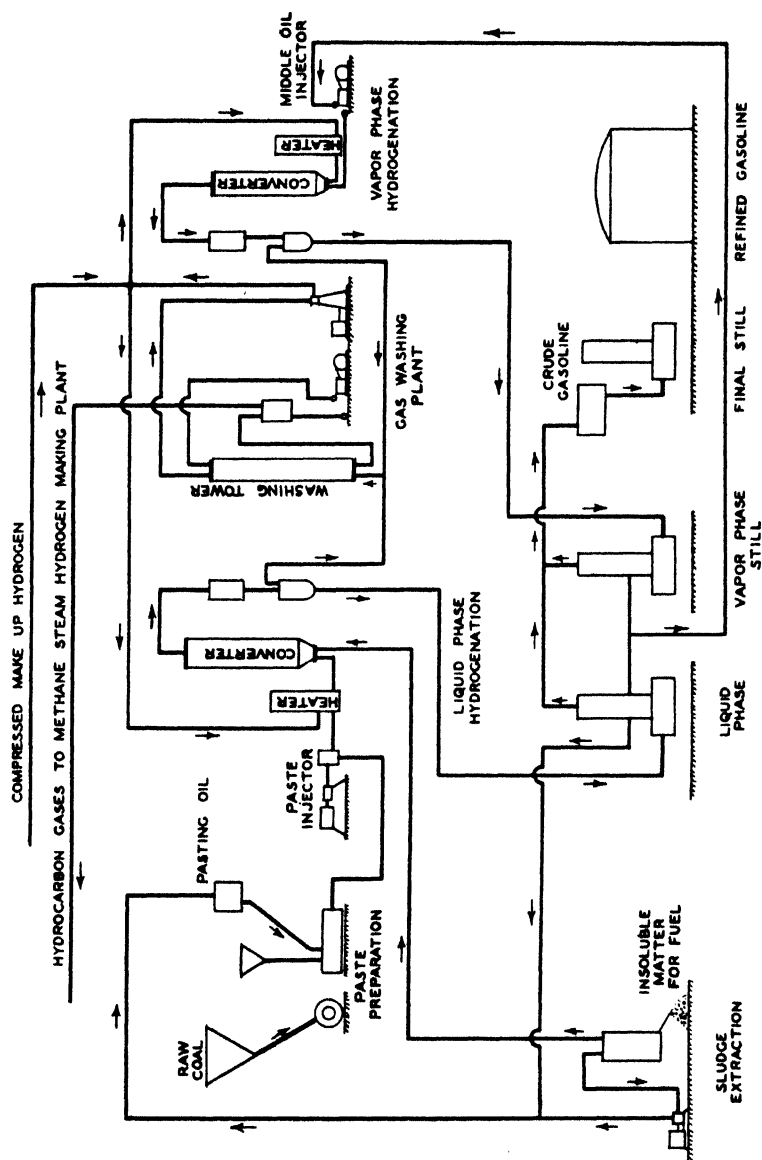


FIGURE 22.—Motor Fuel from Coal Hydrogenation.

High-pressure hydrogenation has developed into an extensive technology for the synthetic production of motor fuels and lubricating oils. The process is being used in Germany for the conversion of coal into liquid hydrocarbons, which consists in treating a mixture of finely divided coal and oil tar in the form of a thick paste at an average temperature of 400–500° and 200–700 atmospheres of hydrogen pressure. The reaction results in conversion of approximately 60 per cent of the coal into oils and tars or products corresponding to synthetic crudes containing high-octane gasolines. The hydrogenation process is also adaptable to the treatment of heavy asphaltic petroleum oils and tars alone.

The plant at Billingham, England, has a rated capacity of 50,000 tons of gasoline from the treatment of coal tars and 100,000 tons of gasoline from the treatment of coal, making a total of 150,000 tons production per annum. The yield of gasoline per ton, based on coal hydrogenated, is approximately one ton for each 1.5 to 2 tons of coal processed, or one ton of gasoline for each five tons of total coal employed for all purposes including power, heat and utilities generally, as well as for charging material. Gasoline of approximately 75 octane has been produced.

A flow diagram of the process for converting coal into motor fuel is shown in Fig. 22.

The hydrogenation process is adaptable also to the manufacture and improvement of many hydrocarbon products. The general process for the treatment of oil by high-pressure hydrogenation may be shown in connection with flow diagram, Fig. 23.

The process of the Standard Oil Development Company<sup>83</sup> is as follows: the charging oil to be treated, together with hydrogen, is pumped into a reaction vessel containing catalyst at approximately 3,000 pounds per square inch pressure. The hydrogen may be produced by any suitable process, for example, by the treatment of methane (natural gas) with steam and subsequent reaction of the carbon monoxide with water to produce additional hydrogen after removing the carbon dioxide. The oil and compressed hydrogen are mixed and delivered through heat exchangers to a heater and then to a catalyst-containing reaction vessel. The degree of hydrogenation is controlled by the operating conditions. The products and unconverted materials are passed from the reaction chamber to heat-exchangers and coolers to a high-pressure separator in which the liquid product is separated from the gases. Unconsumed hydrogen may be re-used. Runs as long as 12 months have been made.

High-pressure hydrogenation produces, according to Murphree, Gore and Brown,<sup>89</sup> high-quality aviation naphthas from a variety of petroleum stocks at conversions of 50 to 75 per cent per pass with yields of 80 to 95 per cent. The aviation naphthas possess volatilities capable of meeting the specifications of most countries and suitable for blending with high-octane addition agents. The ultimate yield can be increased by reducing the volatility. The aviation naphthas produced by hydrogenation are high in octane rating and possess excellent lead susceptibility. They are free from gum and stable in long-time storage, of excellent color, and extremely low sulfur content. It is stated that the commercial scale hydro-

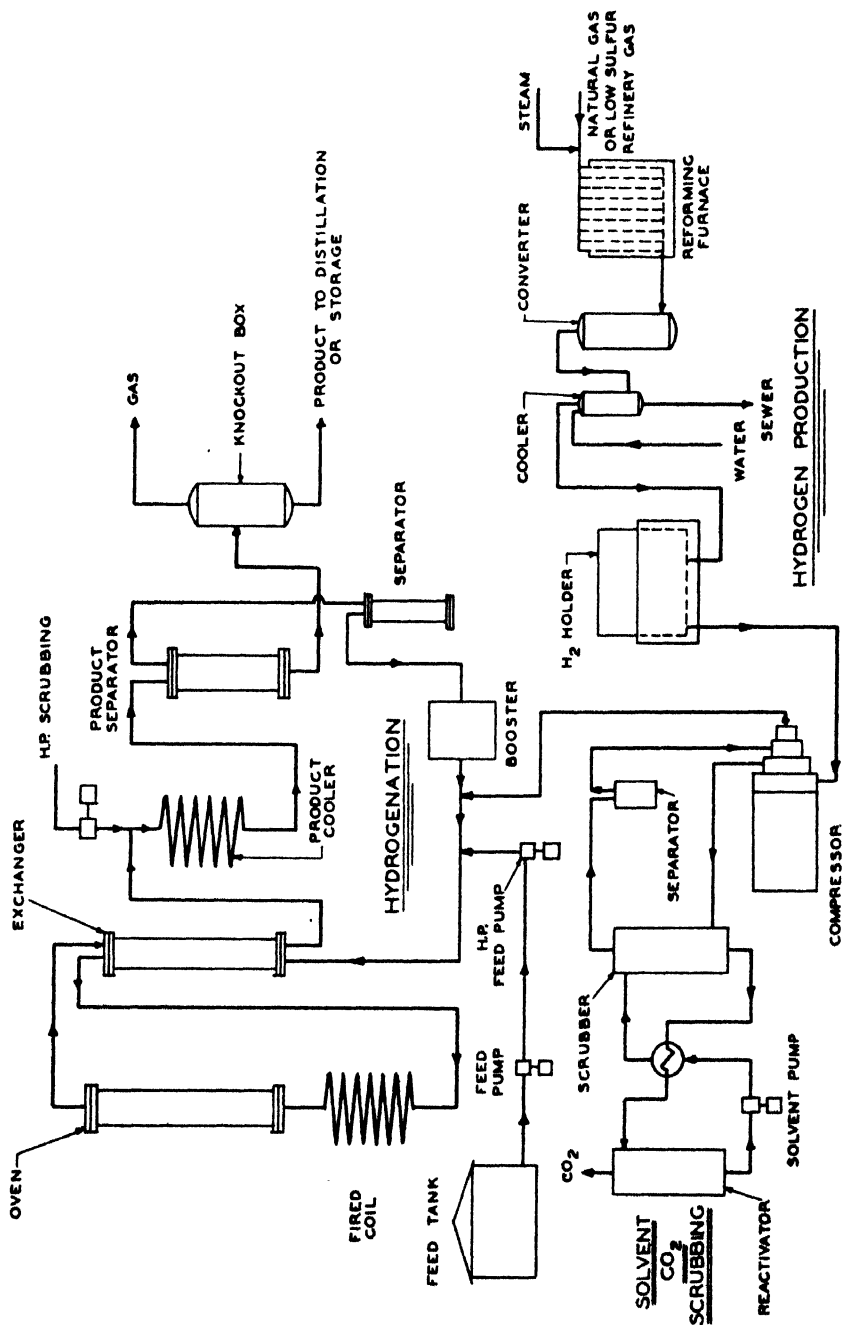
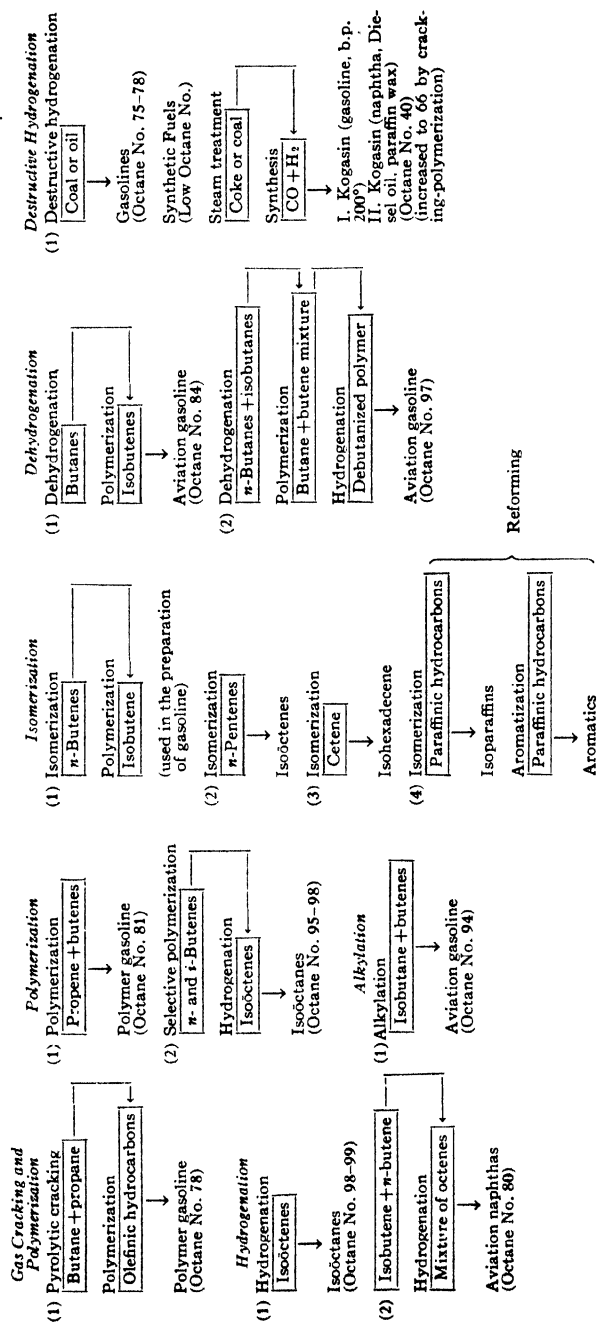


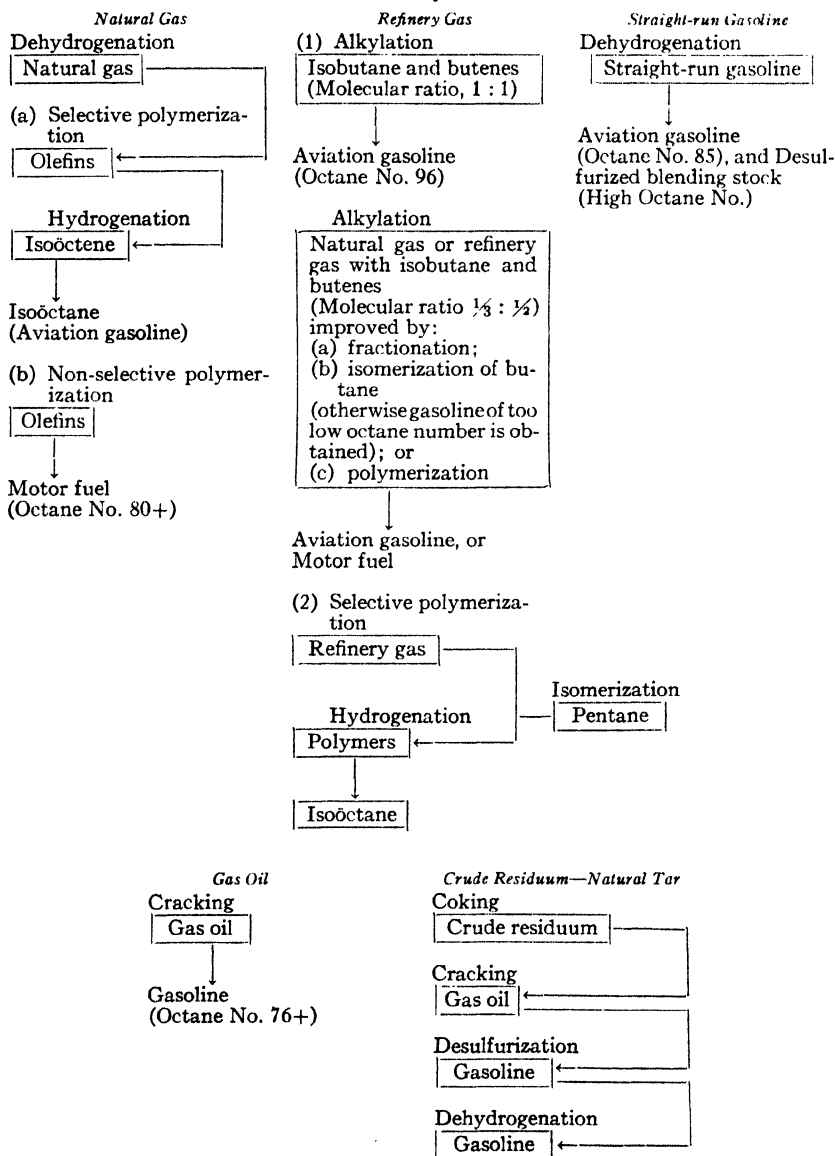
FIGURE 23.—High-pressure Hydrogenation Process.

Table 2. Commercial Catalytic Methods for the Preparation of Motor Fuels.



generation of polymers may be conducted in the same type of high-pressure equipment as that employed for aviation naphtha, although different

Table 3. Catalytic Processes.



catalysts may be used. High-pressure hydrogenation makes available increased supplies of aviation naphthas and of hydrogenated polymers for the production of high-octane fuels, which can be used in the production of

100-octane gasoline to meet the ever increasing demands for this type of fuel.

Sweeney and Tilton<sup>88</sup> show the application of high-pressure hydrogenation to the production of solvent naphthas of a higher solvency than straight petroleum products to be used in connection with synthetic resins for varnishes, lacquers, and similar coatings. They point out that these hydrogenated solvents are superior to the usual petroleum solvent naphthas and compare favorably with commercial coal-tar solvent naphthas, thus meeting the increased demand for these products through the high-pressure hydrogenation process.

Similarly, there is a rapidly developing high-pressure hydrogenation technology in the production of superior lubricants and for the refining and treatment of petroleum products generally to improve their marketability and use.

The hydrogenation process in general is effective in the removal and stabilization of impurities including oxygen, nitrogen, and sulfur derivatives, the net results of the treatment being to produce an oil of higher hydrogen content and more paraffinic in character, thus improving the lubricating qualities, such as viscosity index, high flash, low Conradson carbon, high A.P.I. gravity, and good color, and removing sulfur and other undesirable compounds from motor fuels. Actual performance of the lubricating oils in bus and motor truck service has confirmed laboratory tests.

## SYNTHETIC PURE HYDROCARBONS AND PRODUCTS

### Catalytic Cyclization (Aromatization)

Grosse, Morrell and Mattox<sup>89</sup> developed a catalytic process for converting aliphatic hydrocarbons into aromatics. The great importance of the successful solution of this problem lies in the value of aromatics as high antiknock motor fuels, solvents and as raw materials for explosives (TNT), and a practically endless variety of organic chemicals useful for dye intermediates, pharmaceuticals, medicinals, synthetic resins, and a large number of materials useful to mankind. It is extremely important from the viewpoint that a practically unlimited supply of raw material is available in the form of petroleum *per se*, whereas the present source of raw materials for aromatic hydrocarbons is coal-tar, of which there is only a limited current supply since the production of coal-tar must be geared to coke requirements.

In 1940, about 26,000,000,000 gallons of gasoline will be produced in the United States. If the demand were present, our gasoline output could be increased to over 40,000,000,000 gallons in a short time. Based on this year's gasoline production alone, and using but 20 per cent of the gasoline, the United States of America could manufacture (naturally requiring some time to go into full production) about 33,000,000,000 pounds of picric acid, about 27,000,000,000 pounds of trinitrotoluene, and 25,000,000,000 pounds of trinitroxylyene. There are 85,000,000,000 pounds of high explo-

sives potentially available annually from gasoline within the United States for many years to come.

Various solutions of the problem have been attempted by purely *thermal cracking* ever since Faraday's<sup>27</sup> memorable discovery of benzene in 1825. In these investigations it has usually been assumed that the aromatics are formed via the acetylene or ethylene route. However, Grosse, Morrell and Mattox<sup>39</sup> show from a simple consideration of the classical van't Hoff-Le Bel space models of paraffin or unsaturated hydrocarbons with six or more carbon atoms in a row, that they have a natural tendency

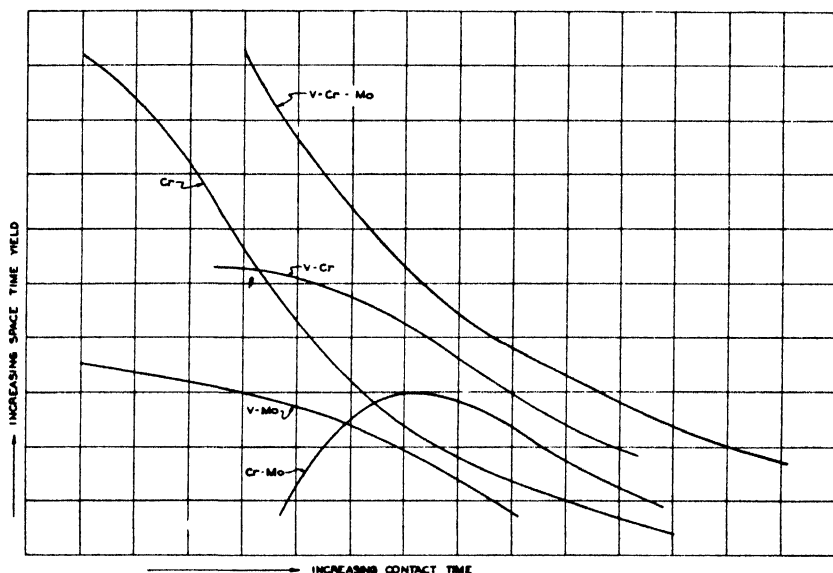


FIGURE 24.—Dehydrocyclization of *n*-Heptane into Toluene with Metal Oxide Catalysts.

to form six-carbon atom rings which, of course, confirms with von Baeyer's strain theory. It is necessary to split off only two hydrogen atoms from two end carbon atoms of the open ring to form a cyclohexane ring which, by further dehydrogenation, is converted into an aromatic hydrocarbon. The conversion of *n*-heptane into toluene is illustrated in Fig. 24 and two practically equivalent mechanisms are indicated.

Grosse, Morrell and Mattox developed efficient and practical oxide catalysts containing, in order of their effectiveness, metals of the fourth, fifth and sixth groups of the Periodic System for the dehydrogenation of straight-chain hydrocarbons to the corresponding olefins. Working with the same and similar types of catalysts along the lines mentioned above, they discovered the new reaction of cyclization.<sup>37</sup>

The new reaction permits the more or less quantitative conversion of aliphatic hydrocarbons containing six or more carbon atoms in a chain into the corresponding aromatic hydrocarbons. For instance, they have been able to convert *n*-heptane into toluene with yields of about 75 per cent of



the theoretical, *i.e.*, 0.75 mole toluene per one mole *n*-heptane, in one pass, or approximately 90 per cent on recycling.

They found that some of the pure oxides which were not supported on carriers, for instance, chromium sesquioxide ( $\text{Cr}_2\text{O}_3$ ) and molybdenum sesquioxide ( $\text{Mo}_2\text{O}_3$ ), produce partial cyclization at temperatures of 450–500°. At higher temperatures they lose their activity very rapidly due to crystallization and are not suitable for practical purposes. The introduction of suitable carriers allows the preparation of active catalysts having a useful life of over a thousand hours.

The catalysts which they used consisted of minor proportions of the oxides of the transition metals of the sixth (chromium and molybdenum), the fifth (vanadium), and the fourth (titanium and cerium) groups of the Periodic System, supported on carriers of relatively low catalytic activity such as, for example, specially prepared alumina or magnesia. Other substances giving no unfavorable reaction with the metal oxides and providing a stable and large surface may be substituted as carriers. The catalysts may be prepared in a variety of ways. Generally, the dehydrogenating metal compounds may be either deposited upon the carriers from aqueous or other solutions, or they may be mechanically admixed with the carriers either in the wet or dry condition.

The principle is always to use such a procedure and only such compounds of the dehydrogenating metal as will finally leave only the oxides of the desired metal on the particles of the support without any interfering constituents. Such compounds are usually water-soluble metal nitrates or ammonium salts of the metallic acid. Chromic acid may be used in the case of chromium.

One convenient laboratory procedure for the preparation of a simple cyclization catalyst containing 8 per cent chromium oxide on aluminum oxide is given here.

Ten- to twelve-mesh granules of activated alumina (Grade A of the Aluminum Corporation of America, sold as a drying agent, is recommended) are impregnated with an aqueous solution of the required amount of chromium trioxide ( $\text{CrO}_3$ ) or chromic nitrate [ $\text{Cr}(\text{NO})_3$ , aq.]. The dried particles are preferably reduced *in situ* in an atmosphere of hydrogen before use.

The carbon or carbonaceous deposit on the catalyst should not be allowed to accumulate in excess of 5 to 10 per cent of its weight. The regeneration is accomplished by burning off the carbon in a stream of air or oxygen-containing gases, its rate being adjusted so as not to allow the catalyst temperature to exceed 900°; the preferred upper limit may, however, be lower.

Greater activities of catalysts and larger space-time yields may be attained with mixed catalysts containing two, three, or even more dehydrogenating metal oxides on the supports. The relationship between the activity and the nature of different metals and their amounts is quite complicated. It is illustrated in Fig. 24 for the specific case of dehydrocyclization of heptane into toluene at 500° by mixtures of chromium, molybdenum

and vanadium oxides on alumina. The sum of the dehydrogenating metal oxide molecules per 100 molecules of alumina was kept constant in all mixtures. All oxides were introduced by means of the corresponding ammonium metalates.

It may be seen in this particular example that at all contact times a vanadium-molybdenum catalyst shows less activity than the corresponding simple chromium catalyst. However, the chromium-molybdenum and, to an even greater extent, the vanadium-chromium catalyst show improved results over the simple catalyst at longer contact times corresponding to higher once-through yields. The triple molybdenum-chromium-vanadium oxide catalyst shows higher activity than the single or any double dehydrogenating metal oxide catalysts.

A large number of pure aliphatic hydrocarbons were cyclized by Grosse, Morrell and Mattox with a variety of catalysts under varying conditions. Among the hydrocarbons used were paraffins, monoolefins and diolefins, and acetylenes. As specific examples may be mentioned *n*-hexane and *n*-hexenes into benzene, *n*-heptane and *n*-heptenes into toluene, *n*-octane and *n*-octenes into *o*-, *m*-, and *p*-xylenes and ethylbenzene. The same catalysts have been used for the dehydrogenation of naphthenic hydrocarbons.

Factors affecting the composition of the products and their yields are the composition of the feed, the chemical composition and physical structure of the catalyst, catalyst activity and life, contact time or space velocity, and the temperature and pressure under which the reaction is carried out. The following example is chosen to illustrate in detail the results obtained by them under one particular set of conditions.

Pure *n*-heptane ( $D_4^{20} = 0.6837$ ,  $n_D^{20} = 1.3879$ ) was dehydrocyclized at 500° over a 6 atomic per cent chromium oxide on aluminum oxide (8- to 10-mesh granules) catalyst at a liquid space velocity of 3.60 volumes/volume catalyst/hour and at atmospheric pressure for a period of one hour. The recovery of the different products in weight per cent of the charge was as follows:

Liquid products ( $D_4^{20} = 0.6922$ , $n_D^{20} = 1.3943$ )	98.1
Gas, uncondensable at 78°	1.7
Carbon	0.17

The gas, 54.1 volumes (at N.Y.P.) per volume of heptane charged, contained 7.1 per cent hydrogen and 2.9 per cent methane and ethane. The liquid product consisted of only a trace (0.5 per cent) of hydrocarbons boiling below 50° (due to the carbon-carbon link splitting) and analyzed 12.1 weight per cent toluene, 11.5 weight per cent heptenes (Bromine No. of product, 16.4), and 75.5 weight per cent unreacted *n*-heptane ( $n_D^{20} = 1.3881$ ). Based on these data, the calculated recycle yield of toluene was about 89 weight per cent, or about 97 weight per cent of the theoretical.

The once-through yields of toluene, gas (mainly hydrogen), carbon, heptenes, and unreacted heptane obtained with the same catalyst at 550° and at different space velocities, are given in Fig. 24. The calculated recycle yields are given in Table 1.

Table 1. Toluene Recycle Yields.

Liquid space velocity (volume/volume catalyst/hour)	0.034	0.195	0.385	0.78	5.00	10.00
Toluene recycle yields, weight per cent of the theoretical (see equa- tion, Fig. 1)	65.7	72.7	78.8	79.5	62.2	60.0

A maximum *once-through yield* of 72 weight per cent of the theoretical was obtained at a liquid space velocity of about 0.39 per hour.

### Synthetic Lubricants

Sullivan, Voorhees, Neeley and Shankland<sup>87</sup> converted olefins to synthetic lubricating oils by polymerization in the presence of aluminum chloride. They have demonstrated the following relationships between the constitution of the olefin polymerized and the properties of the polymerized product.

The longer the straight chain of the olefin treated, the lower will be the temperature-viscosity coefficient of the resulting oil. "In the case of isomeric olefins, the change of viscosity with temperature increases with the degree of branching of the starting material. This cannot be expressed quantitatively, and there are exceptions, as in the case of normal butene compared with isobutene."

The synthetic oils contain no paraffin wax. An oil prepared by polymerizing a cracked paraffin wax distillate was shown to be equal, if not superior, to highly refined natural lubricating oils with regard to oxidation stability, viscosity index, color stability, and comparative lubricating properties.

Isobutene has been polymerized to form polybutenes, resulting in highly viscous liquids, semi-solids, and solids ranging in molecular weight from 2,000 to 400,000. This work was carried on jointly by I. G. and the Standard Oil Development Co. and was presented before the Boston meeting of the American Chemical Society in September, 1939.

The polymerization of isobutene to liquid products using sulfuric acid or boron fluoride as a catalyst was described as early as 1873 by Butlerov and Gorianov. Later work by Otto and Mueller-Cunradi produced a colorless, viscous liquid ranging in molecular weight from 2,000 to 10,000. In the work referred to above, the production and development of polymers ranging in molecular weight from about 25,000 to 400,000 and higher was described. These products are known generically as polybutenes, and may be made either from isobutene or mixtures of isobutene and *n*-butene.

According to the authors, it appears that the properties of polybutenes vary in accordance with their molecular weight. The lower polymers, such as dimers and trimers, are liquids. The intermediate polymers are clear, sticky, and viscous fluids. The higher polymers are ordinarily white, tough, and elastic solids, although colorless in a de-gassed state. The polymers having a hydrogen-to-carbon ratio of two are odorless and tasteless when pure and have a specific gravity of approximately 0.9, subject to slight variations with changes in molecular weight.

The products are very stable and resistant to heat and light, as well as

to strong acids and alkalis at ordinary temperatures. They are also stable toward oxygen and ozone. They are soluble in the hydrocarbons and chlorinated hydrocarbons, but are generally insoluble in oxygenated solvents such as methyl alcohol, acetone, and ethyl acetate, and low molecular weight ethers.

The properties of the polybutenes make them useful for coating high-tension cables, improving the viscosity index of lubricating oils, and for blending purposes where it is desirable to impart their particular properties to the material to which they are added, for example, in greases, textile lubricants, paraffin wax, asphalt, and many other substances. The addition to a paraffin wax, for example, results in reducing brittleness and cracking at low temperatures. Other uses of polybutenes are in motor fuel, cosmetics, and medicinal preparations.

Other methods of making synthetic lubricating oils have been developed, particularly from the treatment of cracked gases, and are briefly referred to below.

Aluminum chloride and boron fluoride have been used by Stanley<sup>34</sup> in the conversion of olefins to synthetic lubricating oils. When operating under pressure and in the presence of these catalysts, it is possible to convert olefins to lubricating oils at temperatures below 100°. High temperatures are usually avoided when polymerizing with aluminum chloride, as this material has a tendency to promote decomposition at moderately high temperatures.

Stanley suggested that the formation of the numerous products by the action of aluminum chloride can be explained on the basis of three types of reactions, namely, (1) polymerization of the reactants to higher olefins; (2) isomerization of olefins to produce the corresponding cycloparaffins, and (3) cracking of the latter under the influence of aluminum chloride to produce light paraffin hydrocarbons and heavy oils less rich in hydrogen.

### Synthetic Resins

The plastics industry, of which synthetic resins are a major branch, is one of the most spectacular because of its rapid growth and the wide variety of uses to which the products are applied, including protective coatings, and molded, pressed, and machined articles of every description. The value of the output of synthetic resins increased from \$8,000,000 in 1924 to approximately \$100,000,000 in 1935. The value of the plastic articles manufactured at present is probably several times that in 1935, with an almost unlimited prospect of growth and variety of applications and uses for the future.

Many of the modern synthetic plastics and resins may be made from raw materials such as acetylene and ethylene, or other substances obtainable from petroleum or natural gas. Synthetic rubber may also be prepared from such hydrocarbons as butenes and pentenes (or butanes and pentanes) which in turn may be obtained from petroleum by cracking or from natural gas.

Synthetic resins have been prepared from olefins and diolefins obtained from cracked petroleum distillates by polymerization with aluminum chlo-

ride and similar heavy-metal solids. These resins have been found to be much poorer in quality than synthetic resins in everyday use.

Among the types of modern synthetic resins are the phenol formaldehyde or phenolic resins, made by the reaction of phenols and xylenols with aldehydes, urea formaldehyde, vinyl, vinyl benzene, vinyl acetate, and vinyl halides, alkyd, glyptal, phthalics, polystyrene, acrylic acid, acrylic acetate, methacrylate, and the various cellulose plastics, such as the acetates, nitrates, ethyl cellulose, and others.

Phenolic resins are made by the reaction of phenols with aldehydes. Benzene employed for making phenols may be made from petroleum hydrocarbons by cyclization and may subsequently be converted into phenols by chlorination and hydrolysis or by the usual method of sulfonation followed by alkali fusion. Formaldehyde is made in large quantities by the oxidation of natural gas hydrocarbons. The phenolic resins are thermosetting, that is, they become insoluble and infusible on heating under pressure. They are also relatively dark in color.

The polystyrene resins are made by the polymerization of styrene, which in turn can be made by the alkylation of benzene with ethylene to form ethyl benzene, with subsequent dehydrogenation by pyrolysis or catalysis to form styrene.

The polystyrene, vinyl and acrylic resins are colorless and thermoplastic, *i.e.*, they soften under heat. They are, therefore, more desirable for some purposes than the phenol formaldehyde and other thermosetting resins, such as the urea types.

The vinyl resins are derived principally from vinyl chloride and vinyl acetate, in some cases by co-polymerization, and may be synthesized starting with ethylene or acetylene as raw materials. Vinyl chloride may be made by direct treatment of ethylene with halogens, followed by sodium acetate treatment. The acrylic resins may also be derived from ethylene or acetylene.

The thermoplastic material, such as cellulose acetate which is widely used for making many molded articles, unbreakable glass, etc., has as one of its component raw materials acetic anhydride, which may be derived from ketene, which in turn may be derived through a chain of reactions starting with propene in cracked gases to form isopropyl alcohol by treatment with dilute sulfuric acid, dehydrogenation of isopropyl alcohol to acetone, and formation of ketene from the acetone by thermal decomposition.

The various plastics and synthetic resins may be employed for different uses with and without fillers and may be cast, molded, laminated and machined into an infinite variety of shapes and sizes.

The milestones in the progress of the plastics industry may be traced from the production of Celluloid in 1875 and casein in 1904 through Baekeland's phenol formaldehyde resins in 1909, and the development of cellulose acetate as a source of plastic materials in 1911. Most of the other resins referred to herein and in the modern industry have been developed, however, during the past two decades.

### Synthetic Rubber

The development of synthetic rubber has been comparatively recent from the commercial viewpoint, even though a considerable amount of this basic material had been produced in Germany during the World War. The foundation for the production of synthetic rubber was made more secure during the past decade in the development of the Buna types of rubber in Germany and in Russia, and in the production of manufactured articles therefrom, such as tires and the more common types of rubber articles.

In the war now going on (1940), difficulty may be experienced in obtaining natural rubber for our own needs. It is reported that the United States has but a six months' supply of natural rubber. The suggestion has been made that rubber trees be planted in a South American country such as Brazil. It would require at least ten years to obtain rubber in this way. Benzene and ethylene, through alkylation and dehydrogenation, yield styrene, a starting hydrocarbon for synthetic rubber manufacture. Butadiene is another hydrocarbon which can be readily produced and converted into synthetic rubber or may be co-polymerized with styrene. The latter type of synthetic rubber has about 30 per cent greater wear quality and strength in tires than natural rubber.

The United States has ample supplies of hydrocarbons in natural gas, petroleum, or coal which can be readily converted into starting materials for synthetic rubber for any conceivable amount desired. The natural rubber requirements for 1940 are about 1,200,000,000 pounds. As already stated, 160,000,000,000 pounds of butadiene are potentially available from natural gas and refinery gases. A like amount of styrene could be produced from ethylene derived from the thermal and catalytic cracking processes by alkylating benzene derived from aromatization of hexane in motor fuel. The polymerization of butadiene and styrene produces a superior synthetic rubber which is potentially available at the yearly rate of over 320,000,000,000 pounds which is about 300 times that of the natural rubber requirements and at a price level competitive with the natural rubber. The United States should make itself self-sufficient from its own natural resources in producing synthetic rubber so that we will not be dependent upon South America or the Far East for our rubber supplies.

The starting materials for the various synthetic rubbers are butadiene, isoprene, dimethyl butadiene, isobutene, chloroprene, styrene, and acrylonitrile. The principal types of synthetic rubbers are Buna, which is a straight butadiene polymer; Buna S, a co-polymer of butadiene and styrene; Perbunan, a co-polymer of butadiene and acrylonitrile, and Neoprene, a polymer of chloroprene, with intermediate types. Other materials have elastic properties, but cannot be considered as synthetic rubbers and, in general, may be looked upon as artificial rubbers. These would include Koroseal, a polymer of vinyl chloride; Thiokol, made by treating ethylene dichloride with sodium polysulfide, and the various polybutenes called Vistanex.

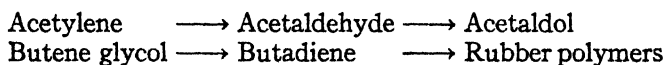
The principal method of diene polymerization employed today is the emulsion process. The earlier method employed was the bulk polymeriza-

tion of butadiene with metallic sodium from which the name "Buna" was derived. The latter process is slow and does not lend itself to the production of co-polymers, and has been abandoned generally for emulsion polymerization. The ingredients are emulsified with water and subjected to conditions of temperature and pressure suitable for converting them into an emulsion of synthetic rubber which resembles somewhat the natural latex of the rubber tree. The emulsion polymerization process proceeds quite rapidly and apparently gives a better orientation of the molecules in a manner which affects favorably the properties of the synthetic rubber product. The resulting product is still unsaturated and the molecular weight is of the order of 150,000. Co-polymerization of butadiene with such substances as styrene and acrylonitrile lend certain properties to the synthetic rubber produced, such as heat resistance, aging qualities, longer wear, better electrical properties, and less solubility in hydrocarbon solvents. Chemically, these co-polymers may closely approach synthetic resins, depending upon the relative proportions of styrene, for example, to butadiene, so that intermediate products of the resin type may be made.

#### Catalytic Dehydrogenation of Monoölefins to Diolefins.

The catalytic dehydrogenation of monoölefins to diolefins has a most important industrial, commercial, and military value, *viz.*, as an economic source of raw material for the production of synthetic rubber. The production of butadiene from butenes and of isoprene from pentenes is the connecting link between the billions of cubic feet of butanes present in natural and cracked gases (also butenes present in the latter), and millions of gallons of pentanes available in natural gasoline and crude oil on the one hand, and the production of synthetic rubber from these raw materials on the other.

The production of synthetic rubber from butadiene and isoprene is well known. Wallach<sup>46</sup> exposed isoprene to light and produced synthetic rubber. Matthews and Strange<sup>48</sup> and Harries<sup>41</sup> independently used metallic sodium to polymerize isoprene to rubber. The Buna rubbers,<sup>50</sup> made on a commercial scale in Germany, are polymers or mixed polymers of butadiene synthesized from acetylene:



Most of the synthetic Buna rubber is not polymerized by sodium, but is produced by emulsion polymerization. Also, the commercial Buna rubbers are co-polymers of butadiene with other materials. Similar developments have taken place in Russia,<sup>1</sup> where ethyl alcohol is used as a source of butadiene. The development of the synthetic rubber industry depends upon the production of cheap butadiene and isoprene, and catalytic dehydrogenation of butenes or pentenes or corresponding saturated hydrocarbons, butanes and pentanes, points the way to this goal. The basic raw materials for the production of rubber now include hydrocarbon oils, hydrocarbon gases, and coal.

Grosse, Morrell and Mavity<sup>40</sup> have described at length their results in

the catalytic dehydrogenation of monoolefins to diolefins. Thus from butene-1 or butene-2, butadiene-1,3 is formed; from straight-chain pentenes, piperylene (pentadiene-1,2), and from branched-chain pentenes, isoprene (2-methylbutadiene-1,3). The original position of the double bond in the framework of the olefins is probably of no consequence since, especially in the presence of the alumina base catalyst, it is freely shifted.<sup>47,70</sup> Thus isoprene was obtained in approximately equal yields from either 3-methylbutene-1 or from a mixture of 2-methylbutene-1 and 2-methylbutene-2. One conjugated diolefin—cyclopentadiene-1,3—was obtained in one operation from the corresponding saturated hydrocarbon, cyclopentane.

The single-pass formation of diolefins from saturated hydrocarbons is not limited to the cyclopentane ring system. In the dehydrogenation of *n*-butane to butenes, small percentages of butadiene-1,3 are produced, the amount depending on the conditions used.

Olefins, whose carbon framework does not permit the introduction of conjugated double bonds, *e.g.*, ethylene and propylene, gave hydrogen and carbon as the predominating reaction. No tendency to form acetylenes or diolefins of the allene type was observed. These observations also apply to the behavior of butadiene-1,3 in the presence of dehydrogenation catalysts. In the latter case the formation of liquid polymerization or condensation products (about 5 per cent) was observed.

Single-pass yields of diolefins from monoolefins up to 20 to 30 per cent were obtained. In the vacuum dehydrogenation of butenes, recycle yields on the order of 60 to 79 per cent are possible.

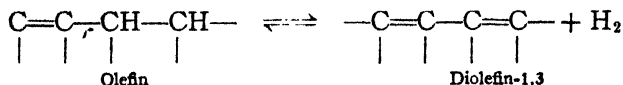
Table 2. Dehydrogenation of Monoolefins to Diolefins.  
(Grosse, Morrell and Mavity)

Monoolefin	Diolefin	Derivative	Melting Point of Derivative (°C.)
Butene-1 } Butene-2 }	Butadiene-1,3	1,2,3,4-Tetrabromobutane High-melting form Low-melting form 1,4-Dibromobutene-2	116 38.5–39.0 52
Straight-chain pentenes	Piperylene (Pentadiene-1,2)	<i>Cis</i> -6-methyl- $\Delta^4$ -tetrahydrophthalic anhydride 1,2,3,4-Tetrabromopentane	60–61 112–113
Branched-chain pentenes	Isoprene	<i>Cis</i> -5-methyl- $\Delta^4$ -tetrahydrophthalic anhydride*	62.5–63.5 <sup>b</sup>
Cyclopentane	Cyclopentadiene-1,3	Maleic anhydride addition product (probably <i>cis</i> -endo-methylene-3,6-tetrahydrophthalic anhydride)	162

\* Neutralization equivalent (by hydrolysis with excess alkali and back titration); calculated for *cis*-5-methyl- $\Delta^4$ -tetrahydrophthalic anhydride, 83; found, 81.

<sup>b</sup> Mixed melting points with a representative sample showed no decrease.

**Conditions:** The reaction chiefly involved may be represented by the general equation\*:



\* This equilibrium for butene-butadiene has been recently investigated by Dementjeva, Frost and Serebryakova in the temperature range of 480–534°.



The olefin in the presence of hydrogen is also in equilibrium with the corresponding paraffin, but this reaction is negligible under the conditions of the present experiments. As is the case with the dehydrogenation of paraffins, the equilibrium of this reaction is shifted to the right with in-

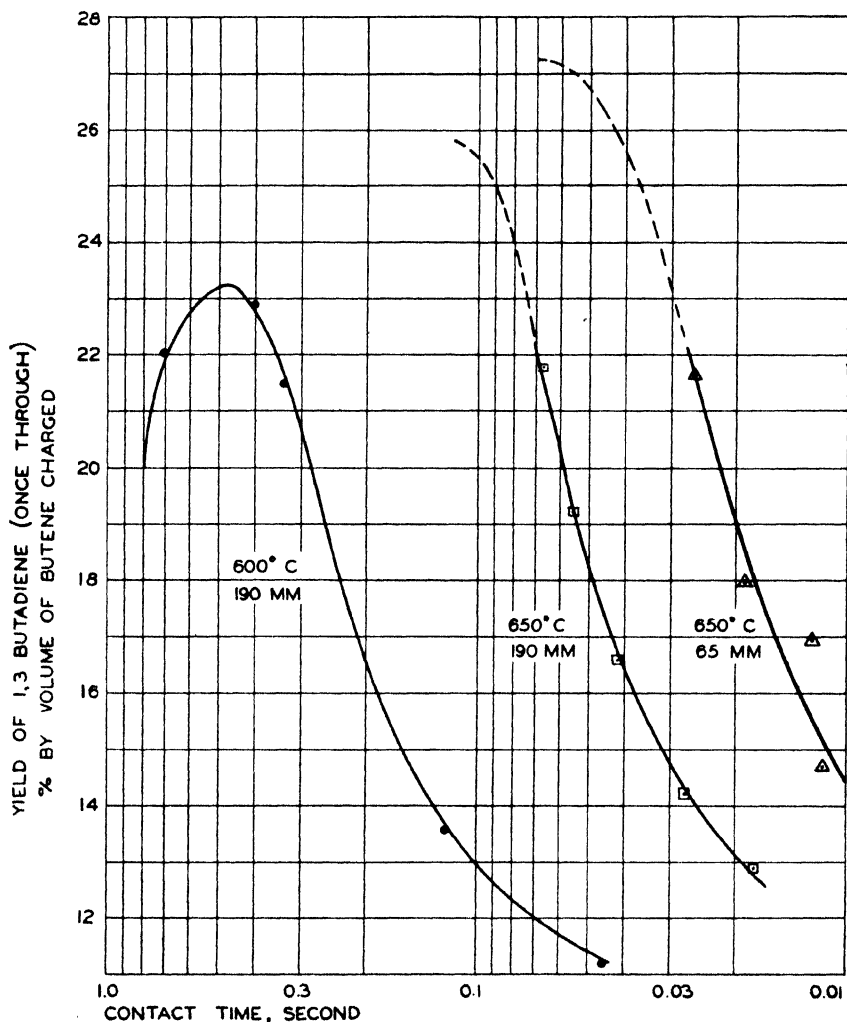


FIGURE 25.—Catalytic Dehydrogenation of *n*-Butenes.

crease in temperature. Moreover, since the reaction to the right represents an increase in the number of moles, it is favored by a decrease in pressure. In view of these considerations, the reactions were performed at reduced pressure, namely, 0.25 atmosphere and lower, and in most cases at a temperature of 600–650°. The results obtained by Grosse, Morrell and

Mavity are shown below, and the yields of the diolefins under the conditions used are given in Table 3.

Table 3. Formation of Conjugated Diolefins by Dehydrogenation.

Monoolefin	Temperature (°C.)	Contact Time (sec.)	Diolefin	Yield Weight Per Cent of Charge	Unre- acted Charge Weight %	Carbon Weight % of Charge
<i>n</i> -Butenes <sup>a</sup>	600	0.75	Butadiene-1,3	18.0	50	11.2
<i>n</i> -Butenes	600	0.34	Butadiene-1,3	20.6	59	4.8
3-Methylbutene-1	600	0.5	Isoprene	21.4	34 <sup>b</sup>	12.8
2-Methylbutene-1+						
2-methylbutene-2 <sup>c</sup>	600	0.39	Isoprene	22.3	44	6.2
Pentene-2	600	0.40	Piperylene	30.3	44	7.6
Cyclopentane	500	1.85	Cyclopentadiene	8.9 <sup>d</sup>	62	8.8

<sup>a</sup> Mixture prepared by dehydration of *n*- and *sec*-butyl alcohols over alumina at 400°. Analysis by Podbielniak fractionation method indicated butene-1, 51.6 per cent; butene-2, 43.3 per cent; propane, 1.7 per cent; residue above butenes, 3.4 per cent. Total olefins by bromine water absorption, 94.5 per cent.

<sup>b</sup> Most of the C<sub>5</sub> olefins recovered were the higher-boiling branched-chain isomers of 3-methylbutene-1. These are included in the 34 per cent.

<sup>c</sup> From the dehydration of *tert*-amyl alcohol over alumina at 400° with 3-methylbutene-1 removed. This mixture boiled at 27.2–37.6° (733 mm.); *n*<sub>D</sub><sup>20</sup> = 1.3915.

<sup>d</sup> The formation of a small amount (2.7 per cent) of cyclopentene is indicated by indirect methods.

These do not necessarily represent the optimum conditions. To obtain these a series of experiments under different conditions was made with *n*-butenes to demonstrate the effect of temperature, pressure and contact time on the yield of butadiene. The once-through yields plotted as a function of contact time† are shown in Fig. 25. These data are also given in Table 4 which includes calculated\* recycle yields. It is readily seen that the dehydrogenation is accelerated at the same contact time† by either an

Table 4. Dehydrogenation of *n*-Butenes.<sup>a</sup>

Temperature (°C.)	Pressure (mm.)	Contact Time (sec.)	Yield of Butadiene-1,3 Volume %		Carbon Weight % of Charge
			Single Pass	Recycle	
600	190	0.75	18.7	37	11.2
600	190	0.7	22	42	
600	190	0.4	22.9	—	5.1
600	168	0.34	21.4	52	4.8
600 <sup>b</sup>	197	0.12	13.5	54	1.5
600	198	0.045	11.2	62	0.8
650	192	0.068	21.8	53	2.3
650	192	0.055	19.3	56	2.1
650	189	0.041	16.6	60	1.4
650	180	0.028	13.3	69	0.9
650	168	0.018	11.9	79	0.5
650	63	0.026	21.8	51	0.9
650	63	0.019	18	60	0.8
650	63	0.013	17.0	65	0.5
650	80	0.012	14.7	69	0.4

<sup>a</sup> For source and composition of butene used in the first four experiments, see Table 3, note <sup>a</sup>. The butenes used in the subsequent experiments were prepared from pure *sec*-butyl alcohol and analyzed 99.0 per cent *n*-butenes.

<sup>b</sup> Average of three experiments.

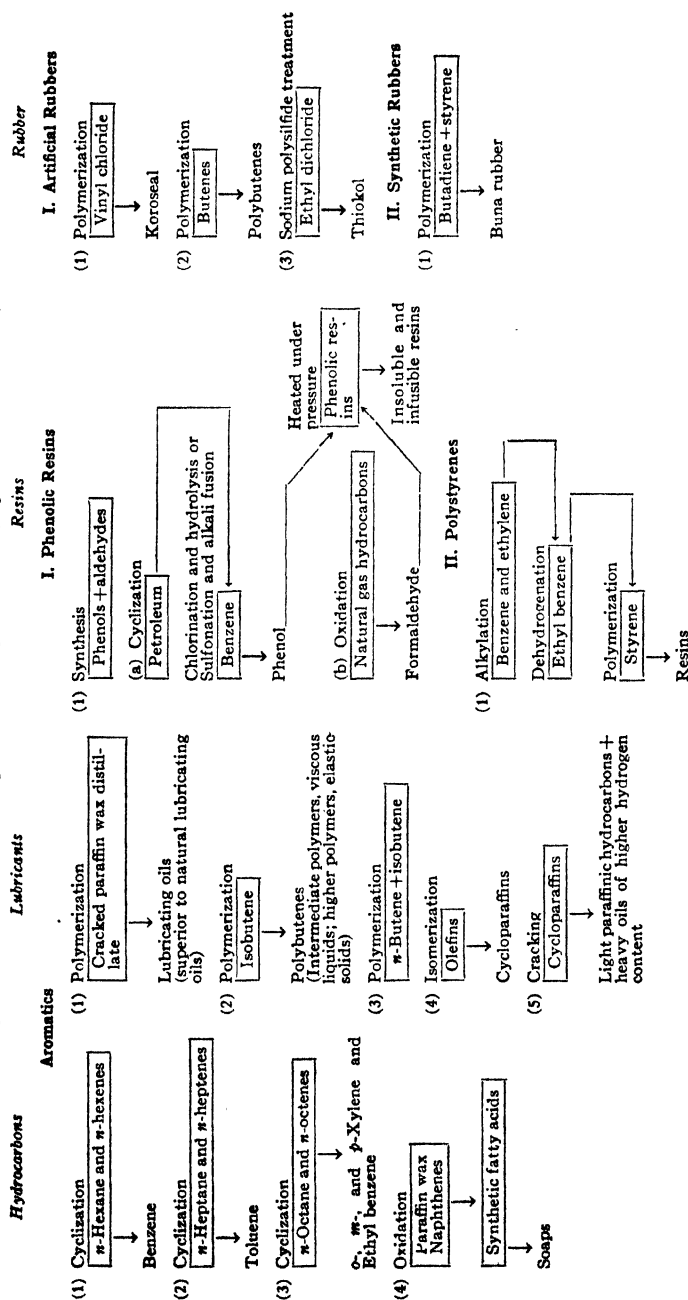
\* Based on analytical data.

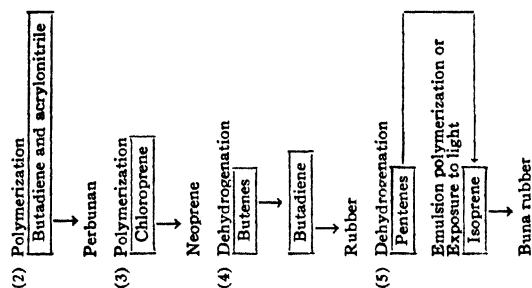
† Contact times were calculated from the equation:

$$CT = \frac{pv}{743(273 + T)(g/M + g'/M')}$$

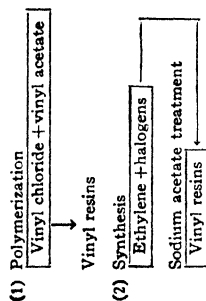
where *CT* is the contact time; *p*, mean pressure (mm. Hg); *v*, volume of catalyst zone

Table 5. Catalytic Methods for the Preparation of Hydrocarbons, Synthetic Lubricants, Resins and Rubber.

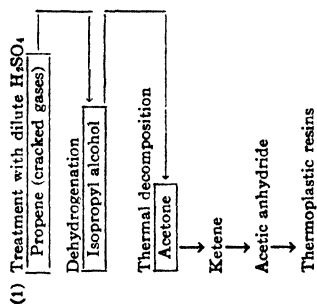




### III. Vinyl Resins



### IV. Thermoplastic Resins



increase in temperature or a decrease in pressure. The best ultimate yields are obtained by recycling at low contact times where the extent of side reactions is small.

*Carbon formation* in the dehydrogenation of olefins is considerably higher than in the dehydrogenation of paraffins, representing over 10 per cent of the charge in some cases (Table 3). This is favored by keeping the reaction products too long in contact with the catalyst and, conversely, can be minimized by operating at short contact times (Table 4). The carbon-forming characteristics of the diolefins are illustrated by an experiment in which butadiene itself was passed over the catalyst.

*Butadiene-1,3* was subjected to the dehydrogenation catalyst at 600° under 0.24 atmosphere pressure and with a contact time of 0.34 second. The products recovered included carbon 16 per cent, liquid products 6 per cent, butane 1 per cent, butenes 20 per cent and unreacted butadiene-1,3, 40 per cent. The liquid, a result of polymerization and condensation reactions, probably contributes to carbon formation. It boiled over a wide range and contained among other products benzene (about 0.5 per cent),<sup>a</sup> styrene (about 1.0 per cent),<sup>a</sup> and a high-boiling hydrocarbon (above 190°) with an intense blue color,<sup>b</sup> similar to that of azulene. Similar results were obtained with butadiene-1,3 at 450° under 0.25 atmosphere pressure and with 3.6 seconds contact time. The products included carbon 12.1 per cent, liquid products 3 per cent, butenes 34 per cent, butane 2 per cent, and butadiene-1,3, 38 per cent. The butenes and butane arise from hydrogenation of the charge with hydrogen formed by decomposition of a portion of the charge.

## CATALYTIC REFINING PROCESSES

### Catalytic Refining of Gasoline

#### Vapor and Liquid Phase

The Gray Process relates to a method of treating mineral oil-hydrocarbon mixtures containing unsaturated constituents which comprises vaporizing the same and passing the vapors outside of the vaporizing chamber in contact with catalytic material heated above the condensing point of the entering vapors without cracking in the presence of the catalyst. More specifically, mineral oil-hydrocarbon mixtures in the vapor state are passed through fuller's earth heated above the condensing point of the entering vapors, thereby effecting a substantial reduction in the objectionable unsaturated constituents. U. S. Patent No. 1,759,812 describes a process wherein the cracked hydrocarbons while in vapor form are passed around the body of adsorptive catalytic material, thus effecting a heat ex-

(CC);  $t$ , duration of run (minutes);  $T$ , average catalyst temperature (°C.);  $g$ , grams of charge;  $M$ , molecular weight of charge;  $g'$ , grams of each recovered product, and  $M'$ , the molecular weight of each recovered product. The free space of the catalyst zone (70 per cent) is taken into account in the constant of the denominator.

<sup>a</sup> Weight per cent of the butadiene-1,3 charged.

<sup>b</sup> This blue color was also observed in the high-boiling liquid fraction from the dehydrogenation of pentene-2.

change. In U. S. Patent No. 1,759,813 a further improvement was introduced in the use of a solvent to activate or cleanse the adsorbent continuously during passage of the vapors through it. Later improvements were directed to other combinations, involving fractionation, etc.

In the practical operation of the Gray Process the vapors from the still enter the top of the clay tower and pass through the clay. The vapors leaving the bottom of the clay tower may then pass through a so-called knock-out box, to remove entrained liquid or polymers, and from there through a fractionating column, condenser coil and to storage. The undesirable compounds are polymerized and separated. It has been found desirable to introduce a small amount of steam into the clay tower during the operation and also to spray gasoline into the top of the tower to act as a solvent and to assist in washing the clay free from polymers. Two or more towers may be used in series.

Clay treatment generally may be carried out by rerunning the pressure distillate in a separate unit and passing the vapors through a vessel filled with clay. However, it is carried out with greater economy by conducting the vapors direct from the cracking unit through the clay-containing vessel. The treated vapors then pass to a fractionator for complete separation of entrained polymerized material and final fractionation of the desired product prior to condensation. The clay-containing towers may be used singly and doubly, both in parallel and in series, and in some cases several towers may be so employed. Where the series flow is employed, the polymer fraction is separated intermediately between the two towers.

According to Foster,<sup>31</sup> the ultimate yield of treated distillate per ton of clay is intimately related to the rate of passage of the vapors through a clay bed, for example, when using 30 tons of clay in a treater the ultimate yield was 6,000 barrels of finished gasoline per ton; when using 15 tons of clay at the same feed rate, 2,400 barrels was the ultimate yield; and when using 7.5 tons, the yield was only 1,700 barrels. This, of course, is related to the time of contact. The process has very little effect on the sulfur content or the sweetening of the gasoline, and the gum content increases with increase in the gasoline yield per ton of clay, although this can be controlled to some extent by periodic steaming and washing of the clay with gasoline.

The process can be operated either by gum control or stream color. The yield per ton of clay will usually be lower when gum is the controlling factor than for color, although this can be offset to a great extent by the use of inhibitors. The yields per ton of clay, color stability and gum content vary with the stock to be treated. Yields as high as 4,000 to 6,000 barrels per ton of clay have been reported with good stocks. However, Price and Brandt<sup>73</sup> report an average of 10,000 barrels per ton of clay used while refining a million barrels of cracked gasoline continuously. Color stability and induction periods decrease with increase in yield. From more refractory stocks the distillate may be acid-treated and distilled through the earth, but some cracked distillates are uneconomical to treat by this process.

Mandelbaum<sup>55</sup> states that, since its commercial adoption in 1924, the

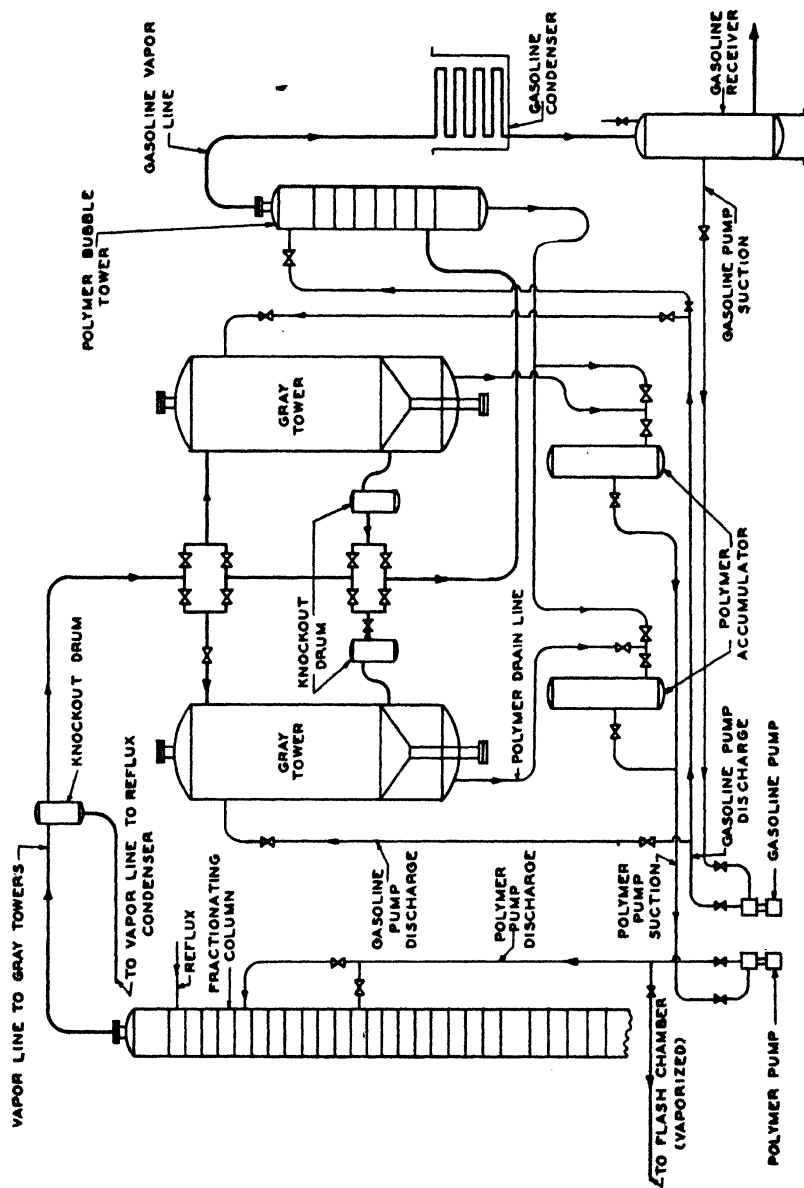


FIGURE 26.—Flow Diagram Showing Series-Parallel Arrangement in the Gray Process.

Gray Process has a treating capacity aggregating 100,000 barrels of cracked gasoline per day. He sums up the rationale of the Gray Process as follows:

- (1) A gasoline fraction is separated from a vaporized cracked distillate;
- (2) the separated fraction, while in vapor form, is brought into contact with an adsorbent having the property of selectively polymerizing the objectionable hydrocarbons;
- (3) the treated vapors and polymers formed are continuously removed from the adsorbent;
- (4) polymers are separated from the treated vapors;
- (5) finally, the treated vapors are condensed.

The adsorbents used are of 60- to 90- or 30- to 60-mesh, the latter being more satisfactory. The best treating material is fuller's earth and similar substances. The reaction is increased by temperature as well as by pressure independently, and the results obtained, expressed in terms of barrels of gasoline per ton of adsorbent treated to a definite standard of quality, are roughly proportional to the absolute pressure. For example, in two neighboring plants, the refining operation in one is carried on at 150 pounds and in the other at 25 pounds. The former treated 6,000 barrels of cracked gasoline per ton of fuller's earth, while the lower-pressure plant has not successfully refined more than 1,200 to 1,500 barrels per ton. Further, according to Mandelbaum, a relatively short time of treatment will suffice, but excessive contact will not cause over-treatment. The vapors passing to the Gray towers may come directly from the cracking process or from a rerun distillation unit. The towers may be arranged in series or parallel, the series flow being preferable. Where the hydrocarbons come direct from a cracking unit containing a large amount of gas, the treating capacity of the adsorbent is quickly depreciated. For this reason vapor-phase-cracked gasoline is more conveniently refined after condensation of the distillate by rerunning through the treating plant. Gray plants are so designed that from 5 to 10 per cent of the gasoline produced is condensed in or returned to the treating tower to aid in washing the polymers from the clay. The gasoline portion of the polymer fraction is vaporized and recovered. Color and gum tests of the treated gasoline do not appear to exhibit a gradual depreciation, but remain at quite constant levels. At 1,000 or 3,000 or 5,000 barrels per ton or more, depending upon the gasoline being treated, they become erratic and the gum rises rapidly. Adsorbents of the type used in Gray treating have, under the conditions maintained for vapor-phase refining, little effect on the sulfur compounds present. This makes a supplementary treatment necessary in the case of sulfur-bearing cracked distillates.

Fig. 26 shows a flow diagram of the Gray Process (Mandelbaum<sup>58</sup>), and Fig. 27 is a photograph of a Gray installation connected to a cracking unit.

Another interesting commercial development in the treatment of cracked gasoline is that referred to as liquid-phase clay treatment or hot clay filtration, wherein the oil undergoing treatment is substantially in the liquid phase while in contact with the adsorbent earth or clay employed.

Another variation in the use of clay for treating gasoline has been described by Willson,<sup>100</sup> in which a slurry of finely divided clay is introduced



into the top of a fractionating column to flow downward over pans counter-current to an ascending stream of vapors undergoing fractionation. The slurry is made in the condensed and finished overhead product. The clay gradually works down through the tower and is removed from the bottom with the reflux into a settling tank from the bottom of which the wet clay passes to a closed tank heated by still bottoms, the vapors returning to a primary fractionator together with the vapors from the original charge.

The process is used by Imperial Oil Refineries, Ltd. at Sarnia, Ontario, and is claimed to be continuous. If the clay tower shows signs of plugging, the slurry is stopped and only overhead distillate is returned. The clay

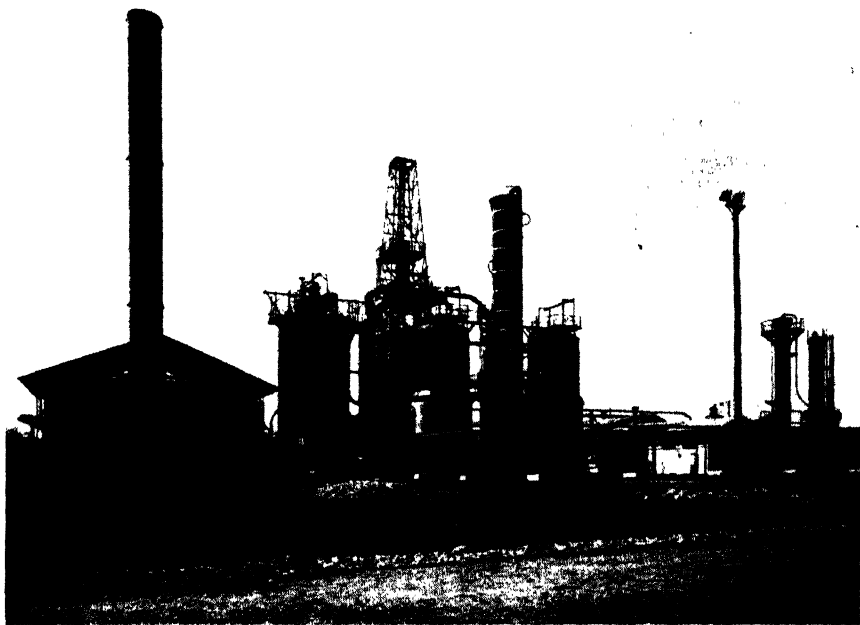


FIGURE 27.

consumption is 3.5 pounds per barrel of 210° end-point gasoline. Less clay is required for reducing gum than is required for producing color stability.

Several patents referring to this general development are: Cross, U. S. Patents No. 1,654,581 (January 3, 1928) and 1,760,585 (May 27, 1930) and Delbridge, U. S. Patent No. 1,682,603. In another process the adsorbent is mixed with the oil and the mixture heated to the appropriate temperature and pressure to obtain the desired treating effect. United States Patents relative to this are Prutzman, No. 1,653,735, and Osterstrom, Nos. 1,894,323, 1,897,328, and 1,930,597.

In one typical commercial operation using the liquid-phase clay treatment, which was studied by Morrell and Egloff, the simplified apparatus shown in Fig. 28 was employed. The distillate to be treated is heated to the appropriate temperature either directly or by heat exchange, or both,

and introduced into the top of the hot clay filter, passing downward through the clay under such conditions of temperature and pressure as would maintain the distillate in substantially liquid phase. The distillate is withdrawn from the bottom of the treating tower (the temperature may be raised if necessary) and introduced into the fractionator, where it is fractionated into the desired end-point product, which is taken overhead, condensed, and cooled. The bottoms are withdrawn from the fractionator. Fig. 29 shows an installation of this type.

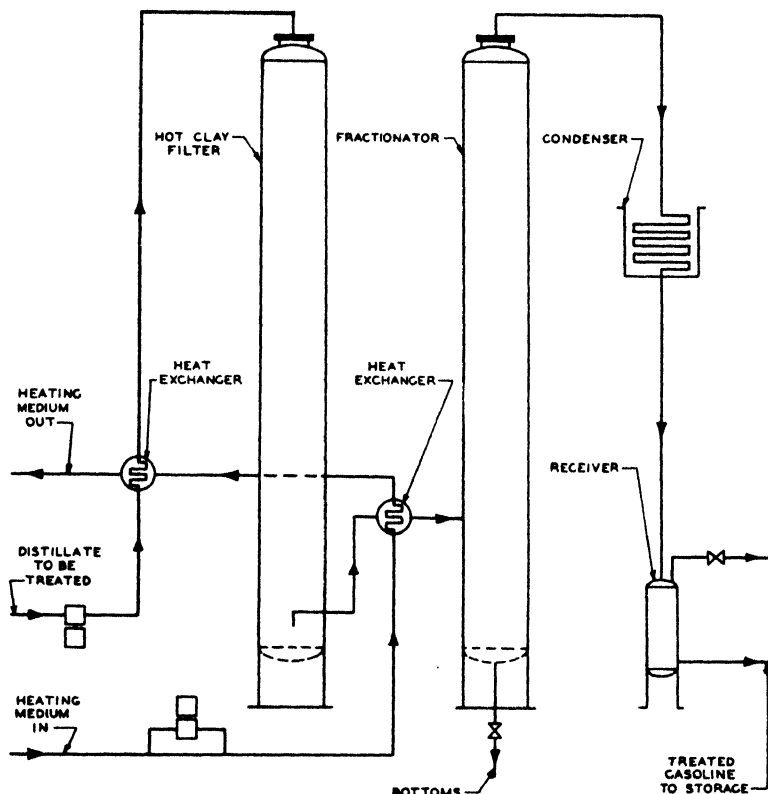


FIGURE 28.—Liquid-phase Clay Treatment.

The following data (Table 1), showing the properties of the pressure distillate undergoing treatment, the gasoline obtained therefrom and the polymers resulting from the treatment, were obtained from a typical run in the equipment described above with a throughput of 5,580 barrels of gasoline per ton of clay.

The finished gasoline had a color of +30 and a copper dish gum of 6 mg. The treating plant was operated in this particular run at a temperature of approximately 210° and 225 pounds. At this point the pressure was gradually raised to 250 pounds and maintained until there was a throughput of approximately 7,330 barrels of gasoline per ton. The color of the gasoline

still remained +30, but the gum in the finished gasoline increased during the last day of operation so that the unit was shut down and the clay re-



FIGURE 29.

moved for regeneration. Increasing the amount of steam employed in the redistillation unit improved the product considerably.

Table 1.

	Pressure Distillate	Pressure Gasoline	Polymers
Gravity (°A.P.I.)	52.1	59.1	32.0
I.B.P. (°F.)	81	74	354
Per cent distilled over:			
5	123	104	392
10	145	118	395
20	191	147	403
30	236	185	408
40	269	219	410
50	309	254	414
—	—	—	—
60	342	279	418
70	370	304	423
80	389	330	432
90	407	360	476
95	424	381	605
E.P. (°F.)	424	391	Cracking
Recovery (%)	95	96.5	—
Color, °Saybolt	Yellow	+30	Dark Amber
Octane No.	69.5	71	—
Copper dish gum, mg./100 cc.	400+	—	—
Induction period (min.)	—	150	—
Sulfur (%)	.18	—	—

As a further example of the operation of high-pressure clay treaters (liquid phase), particularly on Gyro gasolines, the data in Table 2 are submitted.<sup>93</sup>

Table 2.  
Specification of Charge to Re-Run Unit

	"A"	"B"	"C"	"D"
Gravity	62/70	58/62	50/59	55.5
IBP	65/75	70/90	80/90	87
20	105/115	115/130	150/180	158
50	165/200	210/230	270/310	261
90	360/400	390/410	390/410	404
EP	415/435	420/430	415/430	444
Reid vapor pressure (lbs.)	17-19	14-16	10-12	11.6
ASTM gum	15-50	4-11	6-18	—
Induction period	1¼-1½ hrs.	1½-2 hrs.	1¾-2¼ hrs.	—
Octane no.	73-74.5	73-75	65-69	68.7
Color	Yellow	Yellow	Yellow	Yellow
<i>Operating Conditions</i>				
Temperature	520-600° F.	460-550° F.	510-540° F.	500-600° F.
Pressure (lbs.)	750-800	1000	950-1000	500-1000
Rate (bbls./ton/hr.)	34	25-28	14	26-32
Yield (bbls./ton earth)	2000-3500	4500-6000	1000	2000-6000
<i>Specifications Finished Gasoline</i>				
Gravity	66/70	60/63.5	55/60	57.5
IBP	70/80	75/83	85/90	84
20	110/120	115/130	160/185	153
50	170/200	190/220	280/310	248
90	355/390	365/380	365/380	370
EP	390/400	400/410	400/408	399
Reid vapor pressure (lbs.)	16-18	15-16	9-11	11.2
ASTM gum	1-3	1-1.6	100-175*	26.2†
Induction period	4-5 hrs.	4-6.5 hrs.	4½-7 hrs.	4 hrs.
Octane no.	73.5-74.5	73-75	68-69	68.9
Color	17-25	22-28	26-30	22-24

\* Copper dish gum.

† Porcelain dish gum.

In case "A," the charging stock to the Gyro is normally East Texas topped crude, and occasionally this material is mixed in varying proportions with fuel oil from Midcontinent and Gulf Coast crudes.

In case "B," the charge to the Gyro is generally topped Midcontinent crude, *i.e.*, van Zandt. Sometimes crude, either East Texas or van Zandt, is charged to the units.

In case "C," the charge is a wide range gas oil representing a mixture from Cushing, Seminole, and Healdton crudes.

In case "D," the charge is entirely East Texas topped crude.

The liquid-phase clay process is coming into wide use as it has advantages both with respect to economy and results obtained.

## Desulfurization

Schulze and Alden<sup>80</sup> described a catalytic desulfurization process to improve aviation blending naphthas at the 20th Annual Meeting of the American Petroleum Institute, November, 1939. They showed that the tetraethyl lead response of aviation gasolines consisting of blends of iso-octane base and straight-run naphtha from refinery or natural gasoline sources may be greatly improved by removal of the sulfur compounds from the naphtha. In some cases complete desulfurization of the naphtha could be obtained by passing it over a bauxite catalyst at temperatures of 370-400°. They also showed a considerable saving in iso-octane required for

blending purposes, as well as a corresponding saving in tetraethyl lead. All types of sulfur compounds may be removed, with the exception of thiophene. This process, therefore, lends itself to the treatment of naphthas which cannot be treated by ordinary methods.

The conclusions of the investigators are that the catalytic removal of sulfur from aviation blending naphthas, even when the sulfur content is originally low, has been shown to exert a beneficial effect on tetraethyl lead susceptibility. In the case of one blending naphtha, a pentane-free natural gasoline of high sulfur content and comparatively high octane number, catalytic desulfurization increased the amount of finished gasoline that could be made from a given quantity of 91-octane commercial isoöctane by the following percentages:

Octane No.	TEL (ml.)	%
92	0.5	19.7
100	3.0	27.7
87	1.0	52.2

### Sweetening

The purpose of sweetening a gasoline is to remove hydrogen sulfide and convert mercaptans into disulfide, thus improving the odor of the product. The commonly used reagent, sodium plumbite (so-called doctor treatment), reacts with the mercaptans to form lead mercaptides. This in turn reacts with the elemental sulfur, added or present, to form the corresponding disulfides of the mercaptans and lead sulfide.

Regarding the role of lead sulfide in sweetening petroleum distillates, Wendt and Diggs<sup>98</sup> assigned to it a purely catalytic action in promoting reaction of the mercaptans with sodium plumbite. Morrell and Faragher<sup>65</sup> have shown experimentally that lead sulfide is oxidized to lead sulfate, which dissolves in sodium hydroxide to form sodium plumbite, resulting in the usual sweetening reactions. In order to explain the observation that the consumption of sodium hydroxide is insufficient to account for the reaction involving the formation of sodium plumbite in some cases, Morrell<sup>61</sup> suggests that the sodium mercaptides (mercaptans in the presence of sodium hydroxide) are oxidized in part by the oxygen to form the corresponding disulfide and sodium hydroxide, which reaction takes place simultaneously with that shown by Morrell and Faragher.

Rowsey and Whitehurst<sup>78</sup> have described the use of lead sulfide and sodium hydroxide as a sweetening agent and state that they obtain satisfactory results.

*Sweetening with Copper Salts.* Kennedy<sup>48</sup> desulfurizes oils by heating with solutions of sodium chloride, cupric sulfate and sodium hydroxide. Frash<sup>32</sup> treats hydrocarbon oil by distilling it over copper oxides. Amend<sup>3</sup> agitates the oil to be treated with a solution containing an excess of copper salts. Helling<sup>42</sup> deodorizes and desulfurizes oils with solutions of cupric salts. Walker<sup>95</sup> attempts to desulfurize petroleum distillates by passing the vapors of the same over anhydrous copper chloride. The British patent to Allgemeine Gesellschaft für Chemische Industrie<sup>2</sup> shows the use of heavy metal salts for the treatment of cracked oils, including stannic chloride,

zinc chloride, ferric chloride and copper sulfate. Mantle<sup>56</sup> treats hydrocarbon oil by distilling it over copper oxides. Cross<sup>12</sup> utilizes clays containing adsorbed salts of copper over which the vapors of oils are passed for desulfurizing and deodorizing. Odom<sup>71</sup> desulfurizes oil vapors by passing them over copper wool consisting of extremely fine fibers of uniform size. Ridge and Hodgkinson<sup>74</sup> desulfurize oils with mixtures of copper, cupric oxide and a metal halide. Morrell and Comay<sup>63</sup> disclose the treatment of cracked distillates with solutions of copper hypochlorite. Morrell and Faragher<sup>65</sup> state that the mercaptides of various metals, including mercury, silver, and copper, are formed and react with sulfur to form the disulfide in the same manner as lead. A process similar to Cross, U. S. Patent No. 1,515,733, is reported by Eckart.<sup>17</sup> Hounsell<sup>46</sup> describes the use of cupric ammonium hydroxide as a sweetening agent. Morrell and Bergman<sup>62</sup> have shown the use of types of equipment which are suitable for solutions of this type, specifically disclosing cupric chloride. Removal of the suspended and/or dissolved cupric compounds was effected by treatment with small amounts of fuller's earth. Walter and Muhlenberg<sup>97</sup> treat gasoline by agitating it first with ammonium chloride and then with copper sulfate and zinc sulfate. Herthel<sup>43</sup> desulfurizes oils by passing the vapors over anhydrous cupric chloride and then into an alkaline solution of lead salt. Blumenberg<sup>6</sup> uses cupric sulfate and calcium hypochlorite. Greer<sup>35</sup> states that amorphous cupric sulfide readily adsorbs mercaptans and can therefore be used for sweetening gasolines. Straub<sup>86</sup> describes the use of cupric chloride for the treatment of cracked gasoline. The cupric chloride is made up by dissolving copper sulfate and sodium chloride in water. The resulting solution reacts with the mercaptans, forming cupric mercaptides, which react further with the cupric chloride to form the disulfides and cuprous chloride. The cuprous chloride may be regenerated by treatment with hydrogen chloride and oxygen. Straub states that the cupric chloride solution is very corrosive and will attack nearly all metals and concrete. Phillips and Stafford<sup>72</sup> treat oil vapors with sodium hydroxide solution containing dissolved copper oxide. Rostin<sup>77</sup> purifies mineral oils by passing them over heated reduced granular copper. Gray<sup>34</sup> sweetens cracked gasolines by distilling them through copper acetate and then through fuller's earth.

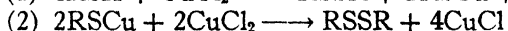
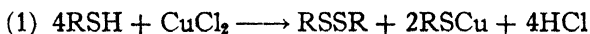
Day<sup>13</sup> describes the use of a mixture of copper sulfate and ammonium chloride for sweetening gasoline, preferably mixed with an earthy adsorbent. Excellent results were obtained by the use of this process as is shown in Table 3. The contact material was prepared by incorporating 25 parts by weight of ammonium chloride and 25 parts by weight of cupric sulfate

Table 3. Properties of Gasoline Before and After Treatment.

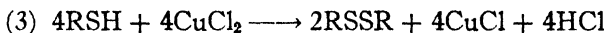
	Before (Sour)	Plumbite- treated	Copper- treated
Color	-9	-5	-8
	-9	-6	-8
Arc stability	Clear	Haze in	Clear
	30 min.	7 1/2 min.	30 min.
Induction period	170 min.	120	180
Induction period + 0.05% inhibitor	270	265	245
Octane no.	69	69	69
Octane no. + 1 cc./gal. TEL	75	75	75

(dissolved in water) with 50 parts by weight of 16–30 mesh fuller's earth and drying at 120°, 30 grams of reagent being used; percolation, downward, at room temperature.

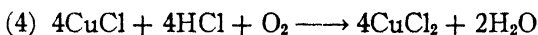
The mechanism of the reaction of mercaptans with the copper sweetening solution is essentially the oxidation of the mercaptans to the corresponding disulfides and the reduction of the cupric ion to the cuprous state. Exemplified with a cupric chloride solution, the reactions are as follows:



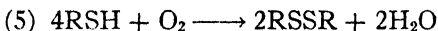
Combining the two stages, the equation becomes:



The cuprous chloride formed in the reaction, although practically insoluble in water, is quite soluble in solutions containing a high concentration of chloride salts. The hydrochloric acid is retained also by solution. These two factors are essential to the process, since in the next step the cuprous chloride and the hydrochloric acid are reconverted into cupric chloride by oxidation with air. The equation for this reaction is:



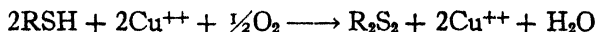
Addition of equations (3) and (4) gives the simple expression:



from which it is seen that no chemicals, other than oxygen, which in practice is obtained from compressed air, are concerned in the process.

Schulze and Buell<sup>81</sup> (Perco) describe the use of a mixture of cupric chloride and sodium chloride, either in an aqueous solution or adsorbed on fuller's earth, following treatment by washing with an aqueous solution of sodium sulfide. The reactions they propose are similar to those described by Straub.<sup>86</sup> The general principle of the treatment with cupric chloride is described above.

*U.O.P. Copper Sweetening Process.* The purpose of the U.O.P. sweetening process is the conversion of mercaptans into disulfides to obtain a product which is "sweet" to the doctor test. It involves bringing light petroleum distillates, either cracked or straight-run, into contact with a solid copper salt. The sweetening reagent acts catalytically with the use of air or oxygen, either continuously or intermittently. The process probably involves the reaction:



It has been shown that cracked gasolines, after sweetening, contain a copper-hydrocarbon complex. This material affects the gasoline properties unless correctly removed. A secondary reagent is required to effect the removal of this complex.

Operation of the U.O.P. sweetening process involves the preliminary washing of the gasoline with a caustic solution to remove the contaminat-

ing impurities, particularly hydrogen sulfide. The gasoline may flow directly from the stabilizer on the Dubbs unit. The caustic wash is accomplished in two stages. It is used for the partial removal of mercaptans and is continuously regenerated with steam.

The caustic washed gasoline is passed through a heat exchanger to be heated to a temperature of approximately 30°. It is mixed with a controlled



FIGURE 30.

quantity of air and passed through a stationary bed of the copper sweetening reagent. Any suitable device, such as an orifice mixer, may be used for bringing the gasoline into intimate contact with air. The air is circulated from the refinery compressor, through a vessel termed a dryer, for the removal of entrained oil and water. The quantity of air is controlled by a calibrated valve. The mixture of gasoline and air passes downward through the tower containing the reagent.

After contact of the mixture with the copper reagent, the excess air is



separated in a receiver; the separator is held at a pressure of approximately 15 to 20 pounds to minimize the loss of hydrocarbons. The gasoline, essentially free from air, passes through a tower containing the secondary reagent. This reagent is required with cracked gasolines to free the gasoline from any copper entrainment. From this tower, the gasoline passes to storage. Inhibitor may be injected into this line.

In the operation of a plant with a single tower, there is an alternate flow of straight-run and cracked gasolines, followed by a short period of air blowing. With the installation of two towers for the primary reagent, a continuous operation is possible, each tower being used alternately. The reagent in the tower not in use is air-blown for a short period. The tower is first filled with straight-run gasoline, after drainage of the cracked gasoline, to wash the reagent free from any cracked gasoline, and the air is then passed through. Otherwise, the cracked gasoline oxidizes with the resulting formation of peroxides and gums. Each of the towers is expected to operate on a thirty-day cycle, after which it will be necessary to remove the copper reagent, remix it, and return it to the tower. The reagent will then be approximately as effective as the new reagent.

The primary towers are protected from the formation of iron chloride. A lining of acid-proof cement gannister or a suitable phenolic varnish has been found satisfactory. A similar protection is also installed in the air separator. No additional corrosion protection is necessary. Operating data show that the corrosion rate in unprotected steel equipment is approximately 0.02 inch penetration per year. The volumetric treating loss in the process should not exceed 0.2 per cent of gasoline. Fig. 30 shows a commercial installation of the copper treating process.

### Antioxidants

One of the important problems in the storage and sale of cracked gasolines is the maintenance of its desirable properties and the prevention of deterioration, particularly in respect to color and gum formation and antiknock properties. The formation of gum-like substances in cracked gasoline is undesirable because it interferes with the operation of the motor from the gasoline tank through the feed lines, carburetor, manifold and intake valves. The formation of color is undesirable mainly from the sales viewpoint. The deterioration of the antiknock properties is objectionable, since it reduces the available energy in the gasoline under high pressure combustion conditions. This deterioration generally is associated with oxidation phenomena occurring in storage, and a large amount of study has been devoted to it.

In 1852 Schönbein<sup>79</sup> recognized that turpentine, on exposure to oxygen, formed some compounds of strong oxidizing power. In succeeding years, other unsaturated substances were found to react with oxygen and to form highly reactive products. No mechanism of the reaction gained general acceptance until almost simultaneously Engler and Wild<sup>26</sup> published the theory that by direct addition of an oxygen molecule to an unsaturated molecule a peroxide or "moloxide" was formed. In 1904 Engler and Weissberg<sup>25</sup> again presented this mechanism in a review of autooxidation, and

drew evidence to support it from their own work and that of others on a number of compounds, including amylene, hexylene and fulvenes. They concluded that "most unsaturated hydrocarbons add oxygen more or less easily, with primary formation of peroxides and then further reaction products." The work done on autooxidation since this publication has been reviewed by Milas.<sup>59</sup>

Olefinic hydrocarbons differ widely in their reactivity with oxygen. Wagner and Hyman<sup>94</sup> showed great variation in the rates of oxidation of the isomeric amylenes by air in the presence of an oxidation catalyst.

A number of investigators have found that diolefins containing conjugated double bonds oxidize and form peroxides much more readily than olefins of other types. Thiele<sup>89</sup> showed that fulvenes absorb oxygen and resinify with extraordinary rapidity. Birch and Scott<sup>5</sup> stated that conjugated diolefins oxidize much more readily than simple olefins. Cassar<sup>11</sup> reported that his accelerated oxidation test "did not affect simple olefins, but only diolefins." Flood, Hladky and Edgar<sup>29</sup> found that "diolefins as a class are markedly less stable than monoolefins, but the position of the double bonds is important in determining stability. Conjugated double bonds introduce extreme instability, while a compound containing double bonds widely separated is almost as stable as an average olefin." Kogerman<sup>51</sup> arrived at similar conclusions in a study of the hexadienes. Those with separated double bonds did not absorb a measurable amount of oxygen during several months' exposure at room temperature. The isomeric conjugated compounds began to absorb oxygen immediately on exposure, and oxidation continued at a rapid rate. Analysis indicated that in two cases his products were peroxides and in one case a "monoxide" which he believed had formed from a peroxide.

Brooks<sup>7</sup> reported the appearance of peroxides on air oxidation of "unsaturated petroleum oils," and stated that their formation is the most important reaction in gum formation. Kogerman,<sup>52</sup> Mardles and Moss,<sup>57</sup> Story, Provine and Bennett,<sup>85</sup> and Wagner and Hyman<sup>94</sup> confirmed the presence of peroxides in old gasoline. Cassar<sup>11</sup> showed that peroxidized olefins increased the tendency of unstable cracked distillate to gum formation. Yule and Wilson<sup>101</sup> developed a rapid quantitative method for the determination of peroxides in cracked gasoline.

Smith and Cooke<sup>82</sup> obtained evidence of aldehydes in aged cracked gasolines and considered them primarily responsible for the formation of gum. Story, Provine and Bennett<sup>85</sup> detected peroxides, acids and aldehydes in gasoline which was being evaporated in a copper dish and in gasoline exposed to sunlight. They came to the conclusion that "the products of the oxidation appear to be principally peroxides, with acids as the chief end product, making up the gum." Yule and Wilson<sup>101</sup> showed that the peroxide method, which Story, Provine and Bennett<sup>85</sup> used, determined only a small part of the total peroxides in the gasoline. Brooks<sup>8</sup> stated that peroxides, aldehydes, alcohols and ketones "could easily be detected in samples of cracked gasoline which have become slightly oxidized." He reported the identification of formaldehyde, acetaldehyde, propionaldehyde and butyraldehyde in old gasoline. The aldehydes

formed, he believed, by the reaction of peroxides with olefins, and opposed the conclusion of Smith and Cooke<sup>82</sup> that aldehydes are intermediate in gum formation, as he found that addition of aldehydes to gasoline being evaporated did not increase the amount of gum formed. Brooks<sup>8</sup> considered that gum was largely a mixture of peroxides, although the gum formed after a long period of storage contained acidic substances. He also demonstrated the marked influence of oxidized hydrocarbons on gum formation shown in Table 4.

Table 4. Influence of Easily Oxidized Hydrocarbons on Gum Formation.

Expt.	Gasoline	Mg./100 cc.
1	Straight-run gasoline + 2% limonene	46
2	Refined cracked gasoline + 2% limonene	634
3	Refined cracked gasoline alone	7
4	Straight-run gasoline + 5% isoprene and exposed to light 48 hours	52
5	Refined cracked gasoline + 5% isoprene and exposed to light 48 hours	521

Wagner and Hyman<sup>94</sup> also reported aldehydes, acids and peroxides in old gasoline, and while they confirmed the findings of Brooks that addition of simple aliphatic aldehydes to gasoline did not increase its tendency to form gum, they found that crotonaldehyde did accelerate gumming. They also reported the odor of acrolein in gasoline oxidized under pressure. They postulated reactions giving rise to peracids, which they considered the essential catalysts in gum formation. Yule and Wilson questioned this mechanism, pointing out that a sample of gummy gasoline, which had been washed with sodium carbonate and therefore would not contain peracids, has just as great an effect in accelerating gum formation in freshly cracked gasoline as if it had not been washed.

Mardles and Moss<sup>57</sup> stated that "the process of gumming appears to be initiated by the primary formation of organic peroxides and the products of oxidation other than peroxides, namely, aldehydes, ketones, acids, etc., were found to have no accelerating effect on the gum rate."

Hoffert and Claxton<sup>44</sup> have reported that aged benzene containing unsaturated hydrocarbons shows the presence of peroxides, aldehydes and acids. These earlier studies were largely qualitative in nature.

Morrell, Dryer, Lowry and Egloff<sup>67</sup> studied the rates of formation of peroxides and gum quantitatively in a number of samples of gasoline by bomb oxidation and in storage. From these rates some idea of the mechanism by which gasoline deteriorates and gum forms may be obtained.

One of the conclusions which can be drawn from their work is that peroxides are the first products which are detectable when cracked gasoline deteriorates. They form at different rates in different gasolines, and in any one gasoline they build up with time at an increasing rate. As their concentration increases, other changes occur, such as darkening in color, gum formation, loss in antiknock value and in susceptibility to inhibitors. Peroxides decrease the effectiveness of inhibitors, but unless present in high concentration do not prevent their action entirely.

The same authors studied peroxidation of gasoline in relation to its composition by removing certain groups of hydrocarbons and by a study of peroxidation of pure hydrocarbons. The properties of the gasolines were

determined after removal of conjugated diolefins and again after elimination of all olefin hydrocarbons. The oxidizability of the pure hydrocarbons was studied by testing the hydrocarbons singly, blended with one another, and blended with gasoline.

In connection with this work a Pennsylvania and a California gasoline, both untreated and treated, were analyzed, employing the method of Faragher, Morrell and Levine.<sup>28</sup> The bromine numbers were determined according to the modification of the Francis method by adding the bromate solution at 0° as fast as taken up, rather than all at one time. The analyses of the cracked gasolines are shown in Table 5.

Table 5.

	—Pennsylvania—		—California—	
	Untreated	Treated	Untreated	Treated
Unsaturates (%)	36.89	24.50	38.94	29.77
Aromatics (%)	19.81	16.90	13.06	17.83
Bromine no.	64	43	61	54
Induction period (min.)	65	120	445	No break in 40 hr.

No relationship is apparent between the total unsaturated content of these gasolines and their tendency to oxidize, as measured by induction period and formation of peroxides. The remarkable stability of the treated California gasoline, in spite of its high content of olefins, indicates that a large proportion of unsaturated hydrocarbons need not make a gasoline unstable. The properties of gasoline are apparently more dependent on the type of unsaturates present than on their amount. This accords with the findings of Flood, Hladky and Edgar<sup>29</sup> and Wagner and Hyman.<sup>34</sup> Conjugated diolefins were removed from the gasoline by treatment with maleic anhydride, which has been shown to react quantitatively with conjugated diolefins by Diels and Adler.<sup>14</sup> This reagent was used by Birch and Scott<sup>5</sup> in connection with their work, to which reference has already been made. The treatment did not stop the formation of copper dish gum, although in the California gasolines it greatly reduced it. The reverse of this procedure was tried by adding 2 per cent cyclopentadiene to gasoline which had been treated with maleic anhydride, and the induction period was decreased still further. Maleic anhydride treatment, after this addition, restored the induction period to its value where no diolefin was added, although the tendency to absorb oxygen was not eliminated, which indicates that diolefins are not the only hydrocarbons contributing to gasoline instability.

Olefins were removed with sulfur monochloride, in accordance with the procedure of Faragher, Morrell and Levine<sup>28</sup> to remove all unsaturated hydrocarbons. After this treatment the gasolines showed great resistance to oxidation; for example, they were exposed in a bomb for 44 hours at 100 pounds' oxygen pressure per square inch at 100° without any break in the oxygen absorption curve and a slow drop in pressure.

Regarding the pure hydrocarbons, it was found that oxidation of the paraffin hydrocarbons was very slight. Cyclohexane and the aromatic hydrocarbons tested were also difficult to oxidize. Benzene was unchanged, while toluene showed slight peroxidation, which is in accord with

the known tendency of an aromatic side chain to be oxidized more easily than the nucleus.

The straight-chain olefins, by contrast, oxidized rapidly and formed gum. Cyclohexene was also extremely reactive, and indene and limonene were the most easily oxidized of the compounds tested. Apparently under these vigorous oxidizing conditions indene goes to other oxidation products than gum, as very little is found in spite of rapid oxygen absorption. Limonene oxidizes readily, although it is not strictly a conjugated diolefin. Possibly the ready oxidizability of cracked distillates is in part due to compounds having structures related to that of limonene.

Some additional conclusions from this work of Morrell, Dryer, Lowry and Egloff are as follows:

(1) The tendency of cracked gasolines to react with oxygen and form peroxides is attributable in part to conjugated diolefins and in part to other olefinic hydrocarbons. Removal of both gives a product extremely resistant to oxidation.

(2) The tendency of olefins to form peroxides also differs widely among different members of the series, and with any given olefin is greatly influenced by concentration. A gasoline may contain a high concentration of olefins and yet be very resistant to oxidation. In regard to gum formation, these results confirm those of Flood, Hladky and Edgar.<sup>29</sup>

(3) Diolefins and olefins present together form more peroxidic compounds and more gum than when present singly in the same concentration.

(4) Under the conditions employed, the oxidation of paraffins, cyclohexane and aromatic hydrocarbons is zero or negligible.

Dryer, Lowry, Morrell and Egloff<sup>13</sup> studied the rate of formation of peroxides, aldehydes, acids and gums in gasolines of several origins, some unrefined, some refined, some of which contained inhibitors. The deterioration was also studied during storage over a period of a year, as well as in accelerated deterioration in an oxygen bomb.

Peroxide can be detected early in the storage period when no aldehyde or acid and practically no gum are present. The rate of peroxide formation accelerates with time. Aldehyde begins to appear somewhat later and increases more gradually than peroxide. Acid formation begins still later, and acid concentration increases more slowly than that of either aldehyde or peroxide.

Gum begins to appear in rather large amount as soon as considerable peroxide has formed and before any large development of aldehyde or acid. The curve of gum content versus time is similar in shape to the peroxide curve, and the conclusions seem justifiable that gum formation is closely related to the concentration of peroxide, and that aldehyde and acid are products of secondary reactions rather than intermediates in gum formation.

Smith and Cooke<sup>32</sup> made elementary analyses of gum, and concluded that aldehydes formed by breakdown of peroxides are probably of more importance in gum formation than peroxides themselves. Wagner and Hyman<sup>34</sup> also analyzed gum and presented a mechanism of gum formation in which "peracids" from aldehydes were essential catalysts.

Story, Provine and Bennett<sup>86</sup> studied gum formed by evaporation in the copper dish, and concluded that it was largely composed of acids accompanied by unsaponifiable material resembling polymerized aldehydes, ketones or oxides.

Morrell, Dryer, Lowry and Egloff<sup>88</sup> made a further study of the formation of peroxides, aldehydes, acids and gums in typical cracked gasoline, particularly as to their distribution between the volatile portion of deteriorated gasoline, the gum dissolved in it, and the insoluble gum precipitated after severe oxidation. The elemental composition of the gum itself was also determined.

Their study shows that gum formed by evaporation of oxidized gasoline is high in peroxides, aldehydes and acids. Gum precipitated from gasoline during oxidation is quite different in composition from the dissolved gum, a pronounced characteristic being its higher content of acidic substances.

If the total amounts of these oxidation products in fractions of oxidized gasoline are compared, the peroxides are usually found to be largely in the residue, the aldehydes fairly evenly distributed in all three cuts, and acids present in particularly large proportion in the light fraction.

Study of gasoline being evaporated in gum tests showed that peroxide, aldehyde and acid are formed much faster in a copper than in a glass dish. Evaporation to dryness in the copper dish reduced or completely decomposed peroxides, leaving in the gum high concentrations of aldehyde and acid.

As to the mechanism of gum formation, these authors conclude that to contain large concentrations of peroxides, aldehydes and acids, it is not possible to say that any of these compounds are of no significance in the formation of gum. But the facts that peroxides are present in greatest amount, and that they concentrate in the gum to a much greater degree than do aldehydes and acid, support the earlier conclusion that peroxides are the substances primarily responsible for gum formation.

The use of inhibitors or antioxidants is so closely related to the formation of these peroxides, aldehydes, acids, and gum that a statement regarding them is not amiss. The formation of gums with the simultaneous formation of peroxides, aldehydes and acids is undesirable insofar as cracked gasoline is concerned, and may be looked upon as a deterioration process. Some cracked gasolines of high quality, which are satisfactory for use when first produced, deteriorate in storage so that they become dark in color, high in gum and lower in knock rating. Among the many factors which influence the rate of deterioration of stored gasoline, the most important is oxygen. Gasoline out of contact with oxygen or air changes but slowly.

A number of papers have been published on the application of inhibitors to cracked gasoline. Egloff, Faragher and Morrell<sup>19</sup> studied a number of compounds which protected gasolines, prevented color and increase in gum, or arrested drop in knock rating. Flood, Hladky and Edgar<sup>30</sup> showed the effect of an inhibitor on the rates of oxidation of pure hydrocarbons blended with gasoline. Mardles and Moss checked gum formation by the use of

phenol and thymol. Wagner and Hyman (*loc.cit.*) reported gum inhibition by hydroquinone.

Rogers and Voorhees<sup>75</sup> have shown that a number of compounds increase the induction period of gasoline. They emphasized the aminophenols and substituted aminophenols. Rogers, Bussies and Ward<sup>76</sup> tested the effectiveness of some inhibitors in reducing gum formation in stored gasoline.

Egloff, Morrell, Lowry and Dryer<sup>23</sup> made a comprehensive study on the relationship of the structure of inhibitors to their inhibiting effectiveness. These same authors, in a series of papers, studied the correlation of inhibiting action and oxidation reduction potential, storage stability of gasoline, peroxides in gasoline, mechanism of gum formation, and the formation of peroxides, aldehydes and acids in cracked gasoline, as well as other phases of this general subject.

### Color Stability

Brooks and Parker<sup>9</sup> conclude that the yellow coloring matter in cracked distillates is due to the presence of hydrocarbons containing conjugated unsaturated groups, or diolefins of the conjugated type. This is indicated, according to these investigators, by the ease of polymerizing these highly unsaturated yellow constituents by dilute acid, heat alone, fuller's earth, metallic sodium, etc., and by their rapid oxidation to form large proportions of gum. The coloring matter is not due to the presence of impurities containing oxygen and sulfur. The fulvenes are cited as examples of hydrocarbons containing conjugated double bonds which are definitely colored various shades of yellow, orange, and red. As experimental proof that the yellow colors may be due to hydrocarbons only, they cracked a pure paraffin, protecting the distillate from oxidizing influences, and the distillate was found to be of a bright yellow color.

They indicate, however, that color of cracked distillates may also be due to the presence of phenols, which are readily oxidized, since cresols have been extracted from such distillates by preliminary alkali washing.

Brooks<sup>8</sup> stated that the most common cause of the discoloration of gasoline is a trace of acidity. Sulfur dioxide, and sulfuric acid from its oxidation, is the most common cause of this acidity. Oxidation of mercaptans and alkyl disulfide to sulfonic acids may also cause discoloration. Gasolines which have not been acid-treated may develop acidity and discoloration. According to Brooks, the function of steam in redistilling acid-treated cracked gasolines is to take up the sulfur dioxide formed during distillation. Alkalies or oil-soluble bases prevent discoloration.

Egloff, Morrell, Benedict and Wirth<sup>22</sup> made a study of the effect of mercaptans, alkyl disulfides and sulfur on the color stability of gasolines when exposed to an arc light. They consider color stability as divided into two factors: (1) actual formation of color, and (2) development of a milky cloud or haze. The color stabilities of the gasolines were determined by exposing them to light from a carbon arc lamp under controlled conditions. The authors drew the following general conclusions from this work:

(1) Mercaptans had no effect on the color stabilities of Midcontinent

gasolines and slightly decreased the stabilities of Pennsylvania cracked and blended gasolines. They caused color and haze formation in the Pennsylvania straight-run gasoline.

(2) Alkyl disulfides (a) occurring naturally, (b) added as pure compounds, or (c) formed during sodium plumbite sweetening, caused color and/or haze formation in all gasolines upon exposure to light.

(3) Sulfur, added alone or in excess during plumbite sweetening, caused marked color and haze formation in the gasolines exposed to light.

(4) The presence of both sulfur and disulfides in all the gasolines except Pennsylvania cracked gasoline had more deleterious effects upon color stability than when they were present separately.

(5) Contacting sulfur and mercaptan-free gasolines with plumbite solution did not affect their color stabilities.

(6) The haze formed upon exposure of the gasoline to light could be removed by passing through filter paper. Color improvements resulted in all cases. The straight-run gasolines showed very marked improvement, returning to almost the original color upon removal of haze by filtration, showing that the apparent color of the unfiltered gasoline was mainly due to suspended particles. Filtration of cracked gasolines resulted in clarification with but slight improvement in color, showing that the color produced upon exposure was largely due to soluble colored compounds.

Morrell, Benedict and Egloff<sup>66</sup> further investigated the photochemical formation of color, haze, gum and reaction products in gasolines in the presence of oxygen, nitrogen and hydrogen, and the factors involved in the same. The source of light was a carbon arc lamp used in the earlier work. Their general conclusions from this work are as follows:

(1) Refined Midcontinent straight-run gasoline exposed to the carbon arc light in the presence of air or oxygen developed color, gum, peroxides, acids and aldehydes. The same effects were observed with cracked gasoline and blends. The straight-run and blended gasolines developed haze, but the cracked gasoline did not.

(2) The formation of gum, peroxides, acids, aldehydes, and haze did not occur in either the straight-run or cracked gasoline in the dark even in the presence of oxygen, sulfur, or both, and at the same temperature as the samples exposed to the arc light. The reactions are therefore photochemical.

(3) With oxygen and exposure to light, the cracked and blended gasolines formed more gum than the straight-run gasoline.

(4) Elemental sulfur increased the formation of color, haze and gum upon exposure of the gasolines to light in the presence of air or oxygen. Cracked and blended gasolines formed more gum with sulfur present than did the straight-run gasoline.

(5) With nitrogen, carbon dioxide or hydrogen, color and gum formed in the presence of sulfur. Hydrogen sulfide was evolved in all cases.

(6) Haze particles contained sulfur dioxide and trioxide and/or corresponding acids and organic material. Most of the acid formed in the gasoline was found in the haze particles, which could be removed by filtration through filter paper.



(7) Removal of haze by filtration improved the color but did not affect the gum content of the gasoline.

(8) Exposure to light and air of straight-run gasoline from which sulfur and disulfides had been removed resulted in no haze formation and only a slight drop in color.

An extension of this work on gasolines was made on the photochemical formation of color, haze and reaction products in pure hydrocarbons. The hydrocarbons used were *n*-heptane, 2,2,4-trimethylpentane, 2-octylene, diisobutylene, cyclohexane, cyclohexene, toluene, cyclopentadiene, pinene, and limonene.

It was concluded from this work that chemical and physical properties of hydrocarbons, as indicated by the bromine number and refractive index, were unchanged by exposure to light either in the presence or absence of sulfur or *n*-propyldisulfide. The hydrocarbons could be recovered in as pure state as from the original distillation. It may be concluded, therefore, that the reactions resulting in the formation of color, haze, peroxides, etc. under conditions of ordinary air exposure affect only a small amount of the hydrocarbons.

The pure hydrocarbons formed no color or haze upon exposure to light, with the exception of benzene, which became colored in oxygen, nitrogen or hydrogen. Peroxides, aldehydes and acids formed upon exposure of the hydrocarbons to light and oxygen. The olefin, cycloolefin, diolefin and terpene hydrocarbons oxidized more readily than the paraffin, cycloparaffin or aromatic hydrocarbons.

Comparison of the work with pure hydrocarbons and with straight-run, cracked and blended gasolines, with and without added sulfur or *n*-propyl-disulfide, shows that the behavior of the gasolines was such as would be expected of mixtures of various types of hydrocarbons. In general, pure hydrocarbons or gasolines from which sulfur and disulfides had been removed were color-stable in light. The response to sulfur of paraffin, cycloparaffin and aromatic hydrocarbons was similar to straight-run gasoline, except that the straight-run gasoline had higher peroxide numbers in oxygen and formed mercaptans in nitrogen or hydrogen. These differences might be accounted for by the presence of unsaturates in the straight-run gasoline. The response of unsaturated hydrocarbons to sulfur was like that of cracked gasoline. The behavior of hydrocarbons containing *n*-propyl-disulfide was similar to that of gasolines. The disulfides had a less deleterious effect on the color stability of unsaturated hydrocarbons and cracked gasoline than on the stability of saturated or aromatic hydrocarbons or straight-run gasoline.

*Dyes and Color Inhibitors.* A large variety of dyes in respect to chemical types and colors have been employed<sup>21, 54</sup> for gasolines to impart distinctive colors to them and to offset to some extent drastic refining to produce a water-white color.

Where a 25 to 30 Saybolt color gasoline is required, inhibitors may be used to stabilize the color in respect to exposure to sunlight and also to prevent haze formation. Several aliphatic amines have been found satisfactory for this purpose.

*Use of Gum Inhibitors.* A large number of substances may be used as inhibitors, but practically the selection of an inhibitor is a question of economy. Most gasoline inhibitors contain phenolic or aromatic amine groupings, or both. Effectiveness usually increases where more than one hydroxyl (phenolic) or amino grouping is present, or where they are present together, as in aminophenols.

Solubility in gasoline, insolubility in water, volatility and other properties are also deciding factors in the choice of an inhibitor. The inhibitor should impart little or no color to the gasoline.

As examples of results obtained with various inhibitors, the following data may be given (the induction period being measured by the usual pressure bomb accelerated oxidation test) in Table 6.<sup>16</sup>

Table 6. Induction Period and Storage Life (Pennsylvania Untreated Gasoline).

Inhibitor	Concentration (%)	Induction Period (min.)	Storage Life* (months)
Pyrogallol	0.0016	265	17
Wood tar distillate	0.010	230	Over 13
1,5-Dihydroxynaphthalene	0.0020	195	Over 9
$\alpha$ -Naphthol	0.0018	170	9
Wood tar distillate	0.005	150	9
2-Amino-4-nitrophenol	0.0019	130	5
Catechol	0.0014	130	4
Hydroquinone	0.0014	80	6
None	—	60	3

\* Time required to exceed 10 mg. air jet gum (A.S.T.M., former method A).

To show the variation in susceptibility to inhibitors of various gasolines, the data in Table 7 are presented.<sup>53</sup>

Table 7. Storage Life of Inhibited Gasolines.

Gasoline	Concentration Wood Tar Inhibitor (%)	Induction Period (min.)	Storage Life* (months)
West Texas reformed, unrefined	0.025	310	Over 18
	None	40	1
Pennsylvania, clay treated	0.0047	285	Over 19
	None	185	7
Midcontinent, unrefined	0.025	340	8
	None	245	5
Midcontinent, refined	0.025	345	16
	None	205	12

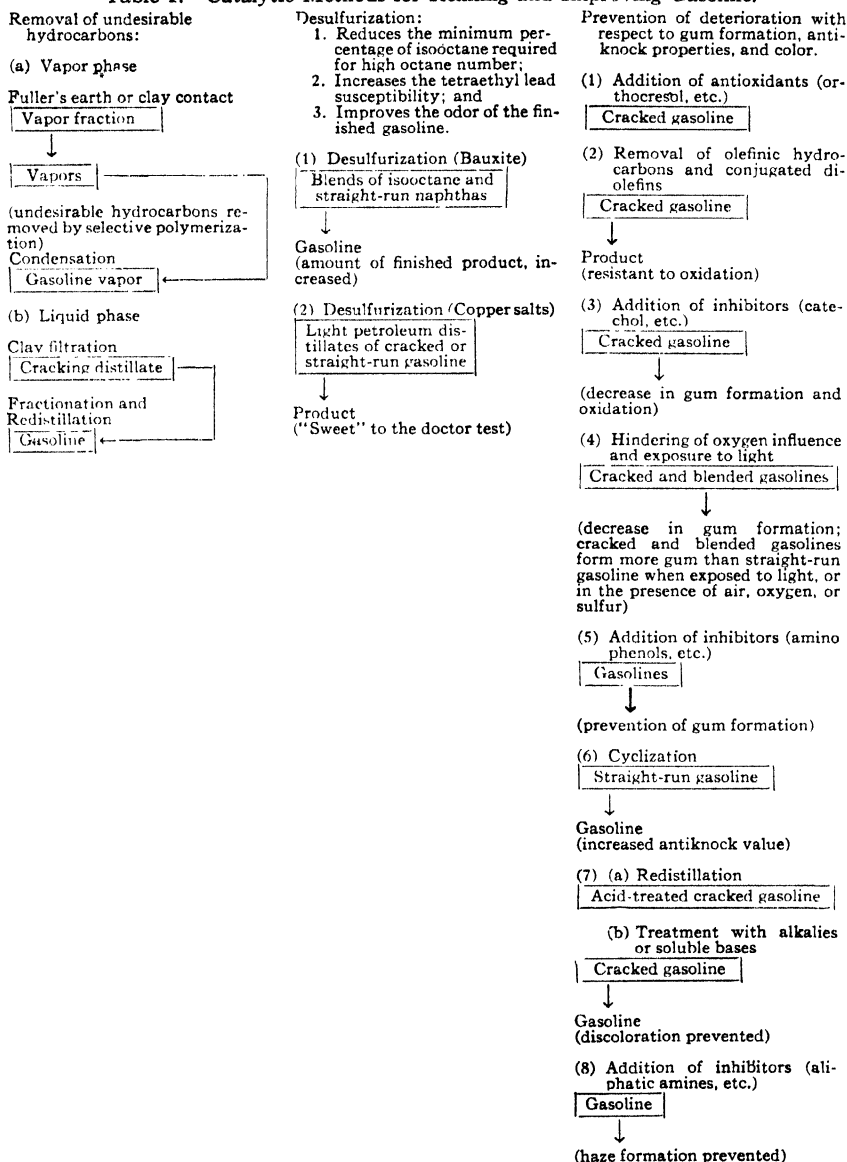
\* Time required to exceed 10 mg. air jet gum (A.S.T.M., former method A).

## SOURCES OF HYDROCARBONS

A comprehensive study of oil production and reserves by the American Petroleum Institute (1935) showed that during the last 35 years estimated reserves of oil have increased yearly above the production of crude oil. For example, 35 years ago the reserve was estimated at one billion barrels, whereas in 1935 it was approximately 13 billions and several large new fields have been discovered since. Scientific and technical progress makes it appear that requirements will be met for many generations.

The major source of hydrocarbons for the future is coal. The conver-

Table 1. Catalytic Methods for Refining and Improving Gasoline.



sion of coal into liquid hydrocarbons may be brought about by either of two major processes which have already been discussed.

(1) High-pressure hydrogenation, wherein a mixture of pulverized coal with oil or tar is converted by destructive hydrogenation into hydrocarbons.

(2) The Fischer-Tropsch process, wherein water gas is produced and then passed over a catalyst to be converted into hydrocarbons.

The use of these methods of conversion of coal into hydrocarbons has been estimated by Egloff and Morrell to produce sufficient motor fuel to supply the requirements of the world at our present rate of consumption for over 25,000 years. This is based on an available supply of coal of 7,400 billion tons and does not provide for the normal uses of coal, which should last over 5,000 years at the present rate of consumption. Hence a division of uses will provide 5,000 years of motor fuel for each 1,000 years of deduction from the use of coal for other purposes. Cracking of tars and oils obtained from coal and oil shales should provide approximately 1,000 years' supply of motor fuel. According to present knowledge, the United States has about one-half of these natural resources. Various tars from lignite, peat and wood, as well as from animals and vegetables, may be cracked to produce motor fuel and other products. The wood tar, vegetable and animal oils represent a replaceable supply. The same method of estimating resources of motor fuels may also be applied to our hydrocarbon resources for synthetic purposes.

It is quite evident from the above discussion that the developments in catalytic hydrocarbon chemistry and technology have prepared us not only for our future motor fuel requirements, but also for an ample and rapid development of a new synthetic organic chemical industry.

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